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FINAL REPORT

CARBON DIOXIDE ADSORBENT STUDY

By Michael Onischak and Bernard S. Baker

SEPTEMBER 1973

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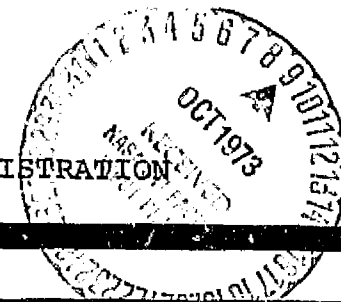
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For

AMES RESEARCH CENTER

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION



**ENERGY RESEARCH CORPORATION**

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ABSTRACT

A study was initiated on the feasibility of using the alkali metal carbonate - bi-carbonate solid-gas reaction to remove carbon dioxide from the atmosphere of an EVA life support system.

The program successfully demonstrates that carbon dioxide concentrations could be maintained below 0.1 mole per cent using this chemistry. Further a practical method for distributing the carbonates in a coherent sheet form capable of repeated regeneration (50 cycles) at modest temperatures ( $423^{\circ}\text{K}$ ), without loss in activity was also demonstrated. Sufficiently high reaction rates were shown to be possible with the carbonate - bi-carbonate system such that EVA hardware could be readily designed. Experimental and design data were presented on the basis of which two practical units were designed. In addition to conventional thermally regenerative systems very compact units using ambient temperature cyclic vacuum regeneration may also be feasible.

For a one man - 8 hour EVA unit regenerated thermally at the base ship a system volume of 14 liters is estimated. An in situ vacuum regenerated unit would have a volume of 4 liters.

The simplicity and effectiveness of the non toxic carbonate bi-carbonate solid-gas system suggest it should be seriously considered for EVA and other life support systems.

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### 1.0 INTRODUCTION

The general purpose of this NASA program is to determine the feasibility of using regenerable alkali metal carbonate reactions to maintain carbon dioxide at very low concentrations in EVA systems. The two carbonates considered in this study are potassium carbonate and rubidium carbonate.

Specific objectives of the NASA EVA application involve the removal of carbon dioxide produced by one man for 8 hours, then regenerating the device at the base ship for repeated use. The concentration level of carbon dioxide in the breathing atmosphere should be maintained below 0.3 mole percent and preferably below 0.1 mole percent. The recirculating atmosphere will enter the device at a temperature between 283 to 294°K at relative humidities of 60 to 80 percent.

For these conditions the feasibility of building a practical carbon dioxide sorber utilizing the gas-solid reaction between carbon dioxide and an alkali metal carbonate has been investigated. This study was concerned with 1) the ability of the reaction to remove carbon dioxide at sufficient rates from low concentration atmospheres, 2) the ability to regenerate the bi-carbonate product in place, and 3) to maintain the reactant's physical structure to produce reasonable cycle life.

Each of these three objectives were successfully demonstrated. It has been shown that the reaction rate in the solid carbonate system is several times greater than required for the EVA system. The latter is always capacity, never rate limited. The reaction product, bi-carbonate, can be readily thermally regenerated at 423°K and evidence also exists that it can be vacuum regenerated in situ at ambient temperatures. Finally, fifty regeneration cycles have been demonstrated experimentally during the program.

A design based on experimental data has shown that a relatively simple compact device could be built for the EVA mission.

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### 2.0 GENERAL BACKGROUND OF GAS-SOLID REACTIONS

In general, gas-solid reactions useful for removing a gas component in an efficient manner must be fast and complete. The study of rapid gas-solid reactions is complicated by many factors. There are two main problems experimentally: first, the true reaction rate must be measured, second, the solid must be made as accessible to the gas as possible at all times during reaction to achieve good absorber utilization.

The true reaction rate, that which is needed in any general design calculation, is not uncovered easily. The most important process masking the true rate is mass transport in the gas and solid phases. Although gas space transport can be handled fairly easily, within the solid, mass transport still exerts its influence on the true reaction rate. This solid phase transport is dependent on the reactants' concentration, the pore size and distribution in the absorber, and surface area which can in themselves be time or conversion dependent.

Hence, to study the true kinetics of a reaction, these effects must be minimized or separated from the basic kinetic process. An experimental method which permits the determination of the true kinetics quickly and simply is of great value. Such a method is adapted to this project using a flat rectangular channel flow reactor. Gas phase diffusion in the channel can be easily separated mathematically from the overall conversion or operationally by increasing the flow rate over the sorbent. The simple geometry of the channel allows quick changeover of various sorbents. A brief description of the apparatus and procedure follows.

Secondly, the effects of slow mass transport within the sorbent should be minimized. Insight gained from previous work (1,2) indicated the necessity of preparing a well dispersed sorbent to approach the maximum of conversion rates. The sorbent's structure is important, not just initially, but throughout the entire course of reaction. A sorbent which is initially effective may plug up during reaction to something quite ineffective if for instance, the product occupies more volume than the reactant. Also, basically due to consumption of the solid reactant, a time decrease of reaction rate appears as had been frequently observed (3,4).

The mathematical analysis of the sorption in the channel by an integral equation analysis (1,2,6) produces flow-independent rates of reaction. The input required for this analysis is simply: the outlet concentration of carbon dioxide from the channel as a function of the channel flow rate. This method was

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first suggested by Katz (7) and has been shown to agree with the conventional reactor analysis (2). Cowherd and Hulscher (8) have also applied this method to liquid flow in a tube for the case when the Leveque solution can be applied.

The alternative experimental apparatus to the channel reactor is the conventional packed bed. This provides more information about the particular bed's conversion characteristic rather than the particular gas-solid reaction. Scale-up is not necessarily straight-forward. However, it is possible to predict the performance of a sorbent in a packed bed from the information obtained from the flowing channel sorber. The conventionally reported breakthrough curves can be predicted. (5)

Studying the reaction by continuous weight gain methods is unworkable for this system because water is simultaneously removed by the reactant for both reaction between the carbon dioxide and carbonate and for hydration of the carbonate.



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### 3.0 TECHNICAL BACKGROUND

The chemical process of interest in this study is  $M_2CO_3 + CO_2 + H_2O \rightarrow 2MHCO_3$ , where M is an alkali metal, in particular, potassium or rubidium. The thermodynamic equilibrium relations of the alkali carbonate - bi-carbonate system (see Appendix B) show this system to be very attractive. Near room temperature virtually complete forward reaction occurs and at moderately elevated temperatures (423°K for potassium bi-carbonate) the regeneration reaction takes place.

An overall rate of sorption is given by

$$r_{ov} = \frac{Q\rho}{60} (\omega_{in} - \omega_{out})/LW, \text{ (g CO}_2\text{/cm}^2\text{ - sec)} \quad (1)$$

where

Q (l/min), is the volumetric flow rate at STP,  
 $\omega$  (g CO<sub>2</sub>/g total), the mass fraction of CO<sub>2</sub>  
 $\rho$  (g total/l), the mass density of the total mixture,  
L, W (cm), the length and width of the surface, equal to 31 cm and 7.6 cm, respectively.

The continuous monitoring of the outlet concentration from the channel yields the rate of removal, and integration of Equation (1) over time yields the fraction converted.

A check of the amount of carbon dioxide sorbed can be obtained from the regeneration immediately following each sorption run. If  $\omega_{in}$  is set equal to zero, Equation (1) can be integrated over the regeneration time to yield the weight of carbon dioxide liberated during the regeneration.

Sorption at low flow rates and from low carbon dioxide concentration streams are flow dependent; that is, the outlet concentration of carbon dioxide from the channel must be corrected for diffusional resistance in the gas space above the sorbent layer. This can be done neatly analyzing the governing differential equations of the sorption section as an integral expression. (1,2)

From a mass balance of carbon dioxide in the sorption section of the channel depicted in Figure 1, the governing differential equation with boundary conditions is integrated to give the basic expression of flow independent rate of sorption R.

As a dimensionless quantity, R is given by:

$$\frac{4}{3} \frac{dC_m}{dx} = R(x) = \frac{a \cdot (\text{actual rate})}{\rho D \omega_{in}} \quad (2)$$

where  $C_m = \omega_{out}/\omega_{in}$ , a dimensionless outlet mixing cup concentration, and

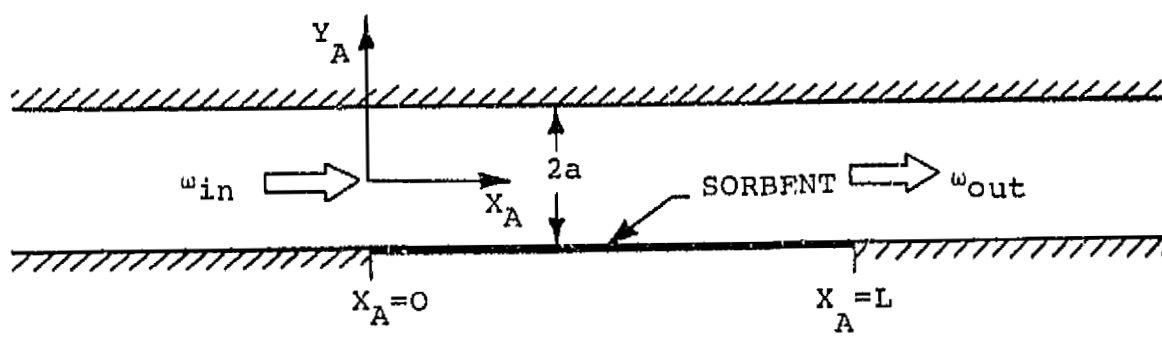


FIGURE 1 SORBENT SECTION GEOMETRY

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$$x = \frac{8}{3} \frac{L}{a} \frac{1}{\text{ReSc}} = \frac{4}{3} \frac{LW}{aDQ} = \text{dimensionless contact time}$$

$\text{Re} = 4a U\rho/\mu$ , Reynolds Number and

$\text{Sc} = \mu D/\rho$ , Schmidt Number for the channel

$D$  = Molecular diffusivity of carbon dioxide in air.

The actual rate, that is the rate unmasked by gaseous diffusion can be obtained using Equation (2) if the behavior of the outlet concentration with flowrate is known. A simple technique that can be used to obtain an analytical relation between  $C_m$  and  $x$  is to fit the data to a polynomial by least squares.

The integral equation analysis provides an independent basis for correcting for gas diffusion in the channel gas space. This can be compared to the conventional differential reactor approach of increasing flow till the conversion obtained is negligibly affected by gas diffusion. Once the effect of diffusion has been corrected then the remaining test runs for various sorbents can be obtained at one high flowrate producing flow independent rates. It is this rate value that can be studied as a function of inlet carbon dioxide concentration, sorption temperature and sorbent composition to produce useful design information.

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### 4.0 APPARATUS DESCRIPTION

The experimental apparatus is shown in a schematic diagram in Figure 2. Various concentrations of carbon dioxide in air can be fed into the channel sorber at different flowrates and temperature. The sorbent held in a support plate is actually a section of one wall of the channel as shown in Figure 3. This channel geometry with one reactive wall provides a well-defined isothermal hydrodynamic system satisfying the assumptions of the classical Graetz Problem. The complete experimental system is shown in Figure 4.

The internal dimensions of the 107 cm long channel are 7.6 cm wide by .24 cm high. The sorbent support pan is machined to hold a sorbent layer 7.6 cm wide by 30.3 cm long, and 0.038 cm thick. Other support pans can be made to hold other lengths and thicknesses of sorbent layers. Detailed drawings of the channel sections are presented in the appendix. The 61 cm entrance region is made to allow higher temperature flows to achieve steady temperature in laminar flow.

A MSA Lira infrared analyzer with a range of zero to 2% carbon dioxide in air has been installed in the system to monitor inlet and outlet carbon dioxide concentration. A second infrared analyzer for water analysis, with a zero to 3% range is also used. Both water and carbon dioxide concentrations were continuously recorded.

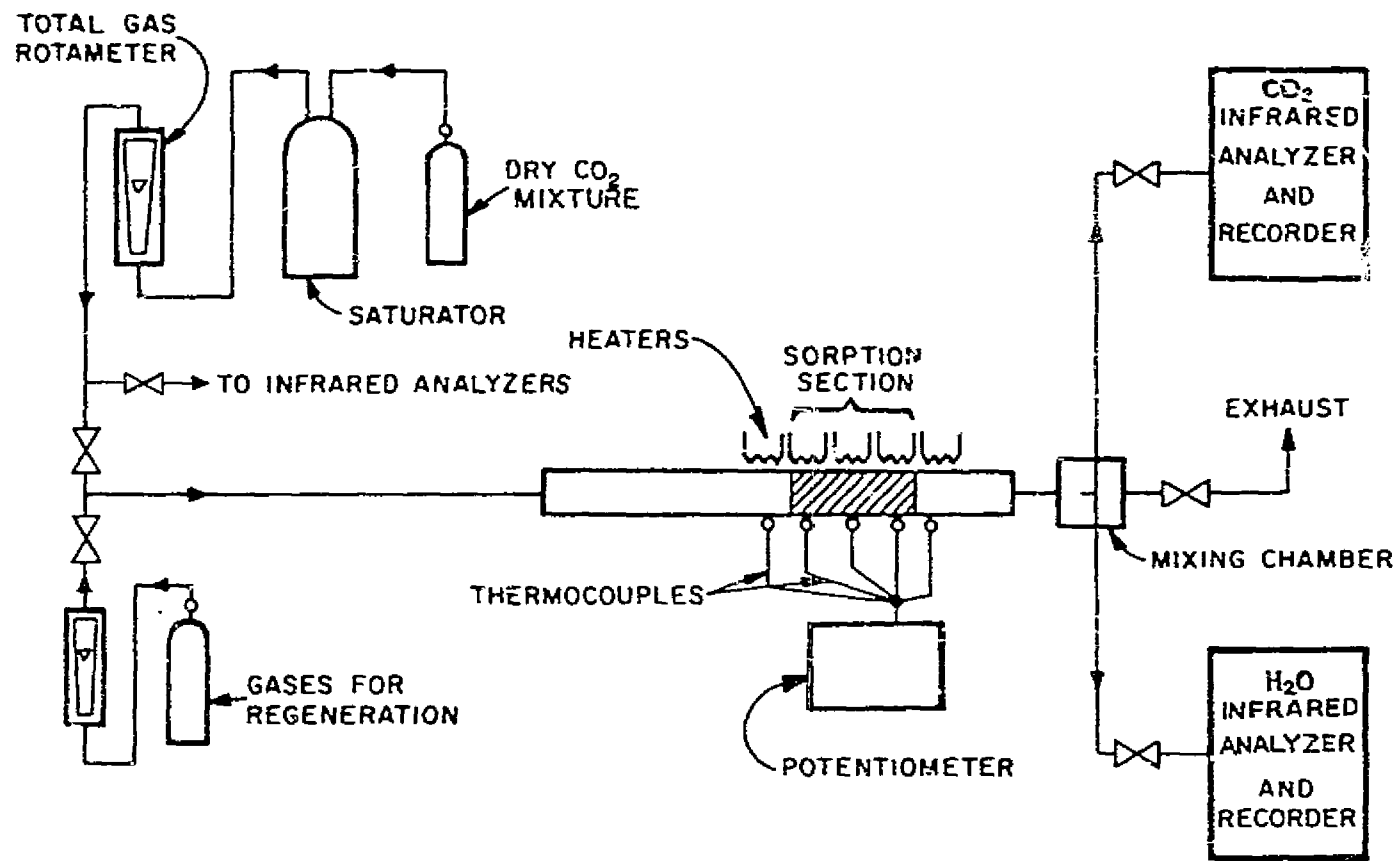


FIGURE 2 SCHEMATIC OF APPARATUS

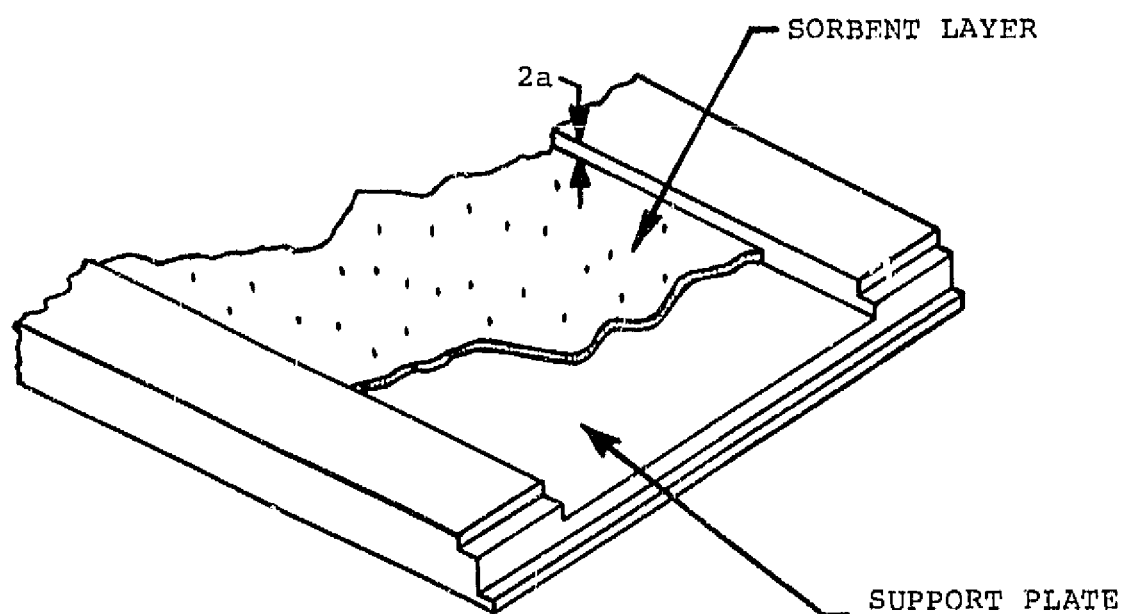


FIGURE 3    SORBENT SUPPORT SECTION

WATER INFRARED ANALYZER

RECTANGULAR CHANNEL  
SORBER

CARBON DIOXIDE  
INFRARED ANALYZER

GAS FLOW  
CONTROLS

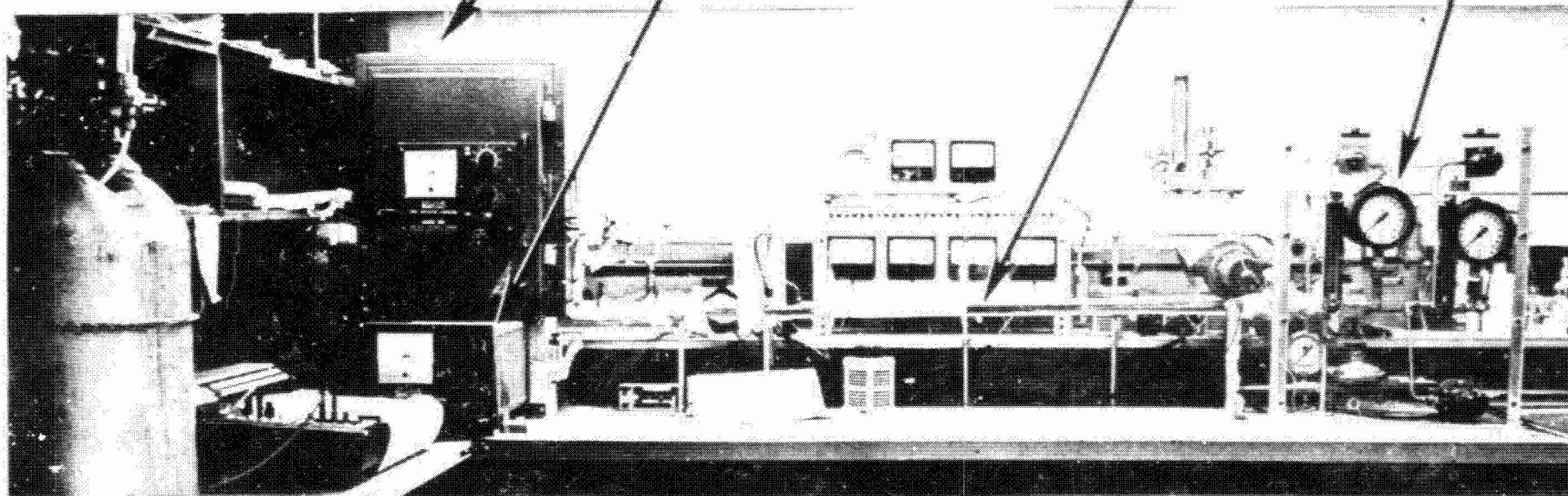


FIGURE 4 EXPERIMENTAL APPARATUS

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### 5.0 DATA CONVERSION

A computer program was written to handle the large volume of raw data generated and to convert it into convenient quantities. A computer output shown in Figure 5 presents the time variation of the rate of conversion of carbon dioxide per weight of carbonate initially present and also per plane area of sorbent. The total weight of carbon dioxide sorbed and the fraction of carbonate converted is also calculated and printed. The experimental flowrate, inlet concentration and sorption temperature are presented as parameters.

The recorder chart record of the measured outlet concentrations from the channel sorber are quickly and easily converted into conversion information for each experimental run.

Sorption experiments were first conducted over a wide range of parameters to isolate the range where practically important data should be taken and to identify any unusual characteristics of sorption of carbon dioxide with respect to the goals of this program.

Experimental runs at room temperature were made with sorbent sheets of various compositions of reactant, support materials, and binder. More extensive sorption data was obtained for the more promising sorbent compositions.



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FIGURE 5

## COMPUTER OUTPUT SAMPLE OF DATA CONVERSION

RUN NUMBER: KCT13-2S

FLOWRATE: 1.15 LITERS PER MINUTE  
 INLET MOLE FRACTION: 2.99181E-3  
 TEMPERATURE: 25 DEGREES CENTIGRADE

TIME OF RUN (MIN)	C(OUT)/C(IN)	---OVERALL CONVERSION---	
		(G CO <sub>2</sub> /G K <sub>2</sub> CO <sub>3</sub> -SEC)	(G CO <sub>2</sub> /SQM-SEC)
.0	.1867	.6541E-04	.3717E-02
1.0	.2378	.6129E-04	.3483E-02
2.0	.2378	.6129E-04	.3483E-02
3.0	.2435	.6083E-04	.3457E-02
4.0	.2717	.5857E-04	.3328E-02
5.0	.2717	.5857E-04	.3328E-02
6.0	.2548	.5993E-04	.3406E-02
7.0	.2773	.5811E-04	.3303E-02
8.0	.2998	.5631E-04	.3200E-02
9.0	.3278	.5406E-04	.3072E-02
10.0	.3557	.5181E-04	.2945E-02
11.0	.4001	.4824E-04	.2741E-02
12.0	.4223	.4646E-04	.2640E-02
13.0	.4555	.4379E-04	.2489E-02

TIME OF RUN (MIN)	INTEGRAL OF RATE GRAMS CO <sub>2</sub>	FRACTION OF CARBONATE CONVERTED
.0	.0000	.0000
1.0	.0047	.0111
2.0	.0095	.0227
3.0	.0143	.0341
4.0	.0189	.0449
5.0	.0235	.0559
6.0	.0283	.0673
7.0	.0329	.0781
8.0	.0373	.0885
9.0	.0414	.0985
10.0	.0455	.1080
11.0	.0491	.1168
12.0	.0527	.1253
13.0	.0561	.1333

RUN NUMBER: KCT13-2R  
 THE RESULT OF REGENERATION IS: 8.00581E-2  
 GRAMS OF CO<sub>2</sub> SORBED  
 OUT OF DATA IN 70

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### 6.0 SORBENT PREPARATION

For any gas-solid reaction system, the structure of the supported solid chemical is extremely important. First, the capacity of the device depends on the optimum utilization of the active material which in turn relates to the way the chemicals are packaged and distributed. Secondly, the intrinsic cyclic ability of the device will depend on the way the reacting chemicals are supported.

ERC has developed a unique and highly effective method of supporting alkali carbonates and other adsorbents so that maximum yield and cycle life are obtained.

A technique had been developed at ERC where the active alkali metal carbonates, dispersed with high surface area materials, are bound together by polytetrafluoroethylene. Sheets of this carbon dioxide sorbent material can be made as pliable as paper down to thicknesses of .005 cm. The optimum sheet thickness would come from a tradeoff between active material utilization and packaging geometry with its auxiliary support structure.

Having sorbents available as sheets permits flexibility in sorber geometry design. These sorbers can have a high ratio of total plane surface area to volume and inherently low pressure drops from the multitude of small channels.

At the beginning of this study, sorbent sheets were prepared in many composition ratios of active carbonate to high surface area support materials to polytetrafluoroethylene binder.

The composition range was quickly narrowed through sorption tests in the channel apparatus and with mercury porosimeter analysis of the sheets before and after reaction. Sorption of carbon dioxide was greatly reduced after several sorption cycles for sorbent sheets above approximately 60% by weight of alkali metal carbonate. Porosimeter tests showed, as expected, the loss of small pores in the sorbent sheet after reaction. The bicarbonate product has a lower molar density than the reactant carbonate, hence it occupies more volume. Upon repeated reaction, the carbonate redistributes itself in more greatly packed groupings yielding poor utilization. This is shown in Figure 6 between an 80% carbonate sorbent after two cycles and a 44% carbonate sorbent after 70 cycles.

Below 30% carbonate by weight in the sheet, the sheets sorb well, however the capacity of carbon dioxide removal was found to be below the optimum. Subsequent tests indicated that the optimum concentration of carbonate in the sorbent sheet was

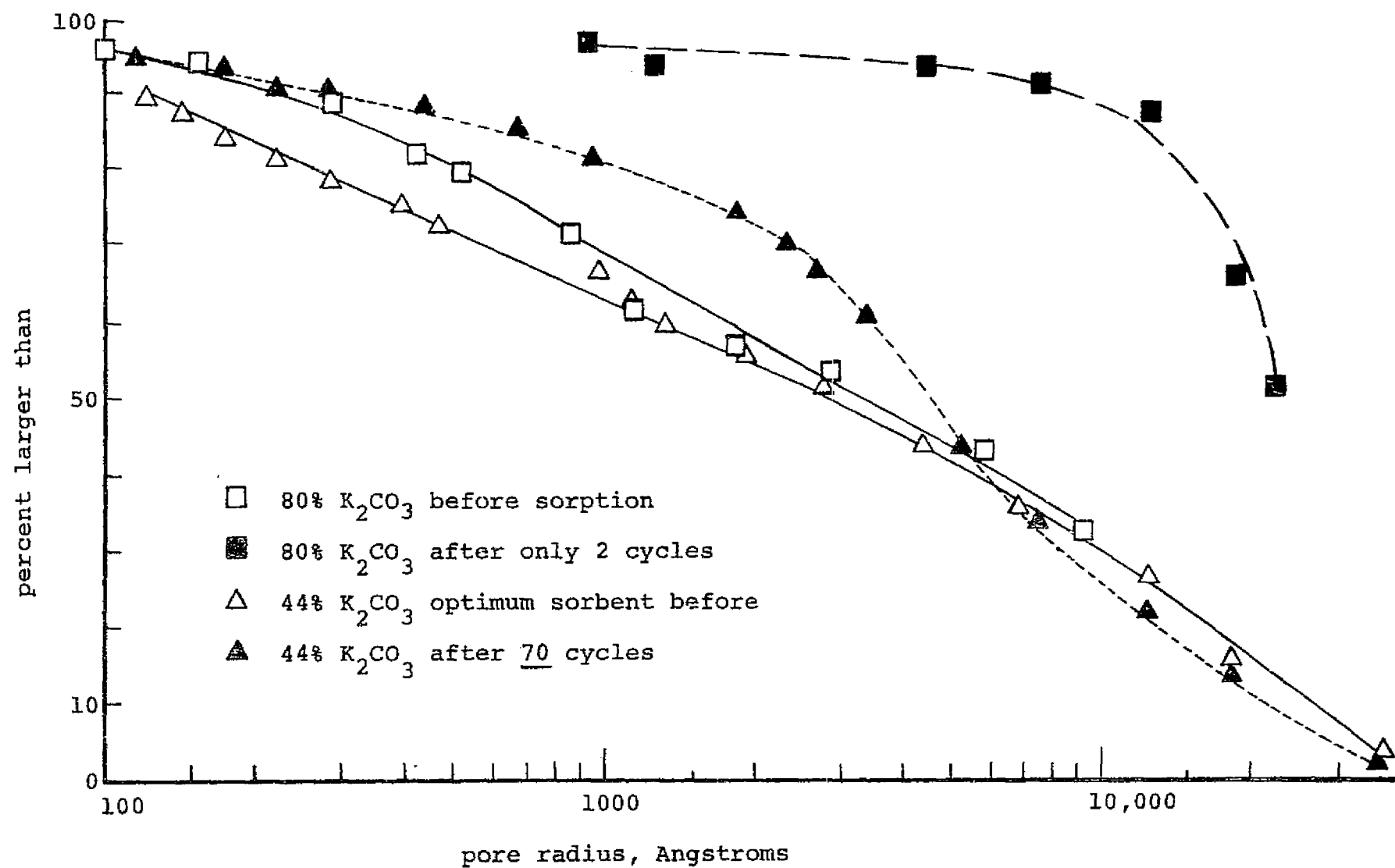


FIGURE 6 PORE SIZE DISTRIBUTION RELATION TO CARBONATE LOADING

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approximately 44% by weight potassium carbonate, the remainder being the support material and binder.

The key for repeated sorption and regeneration of the sorbent sheets lies in their physical structure. ERC's sorbent sheets could be described in terms of a microporosity and a macroporosity. The macropores are necessary to allow transport of carbon dioxide within and throughout the sorbent in terms of a "gas accessibility" to all of the carbonate. This macroporosity is achieved by adding ammonium bicarbonate in the mixing process. At the end of the process the ammonium bicarbonate is removed by thermal decomposition and as it leaves the gaseous products leave large void spaces.

The micropores on the other hand are necessary in terms of reactant utilization or capacity. The product bicarbonate has to have room for expansion during sorption of carbon dioxide. If there are not enough micropores to allow for this expansion any small spaces near the carbonate will close. Closing the fine pores chokes off carbon dioxide from reaching any further, deeper lying reactant.

In terms of measured total void volume, the best performing sorbents have typically 2.5 to 3 cc void space per gram, and 50% of the pores are below 4000 Angstroms.

### Summary Table of Desirable Sorbent Properties

- a. Total void volume on the order of 2.5 cc/gram composed of macro and micropores.
- b. Physical structure maintained throughout cycle life.
- c. Maximum weight of  $K_2CO_3$  per total sheet weight optimized with respect to maximum  $gCO_2$  sorbed/total wgt. and maximum cycle life.

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### 7.0 EXPERIMENTAL RESULTS

#### 7.1 Sorption Tests Of Various Sorbent Sheets

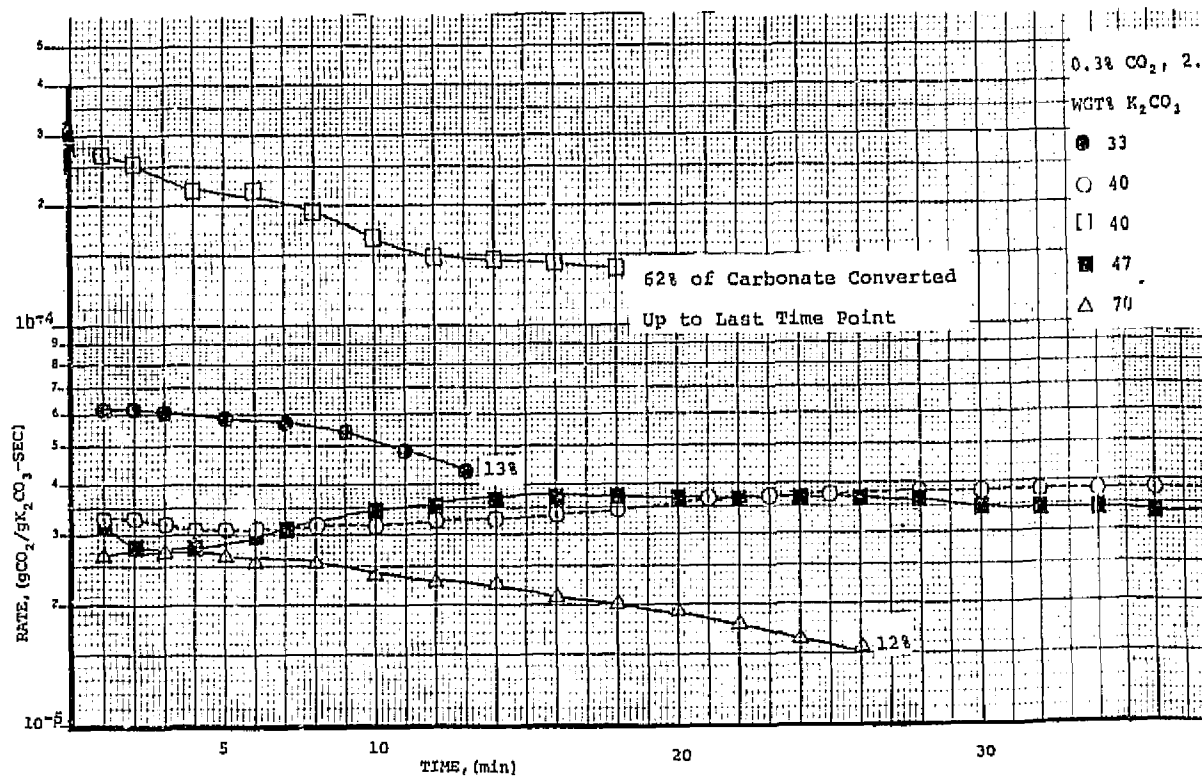
The removal of carbon dioxide under conditions of interest to NASA was first attempted on various sorbent composition sheets exhibiting a large range of carbonate concentration. The results are shown in Figure 7 with the overall or flow-dependent rate calculated from Equation (1). The inlet concentration of carbon dioxide and water vapor was 0.3 mole percent and 2.0 mole %, resp. in air. Sorption took place at room temperature and at various low flow rates that would be indicative of flowrates over each layer in a practical device. The run was stopped when the outlet channel concentration reached 0.1 mole % carbon dioxide.

The results presented in the following figures are for sorbents prepared with potassium carbonate. The study began with potassium carbonate because it is far less costly than rubidium carbonate. Later in the study runs were made with rubidium carbonate sorbents. Sorbents of rubidium carbonate were first prepared as the same composition as the optimum potassium carbonate sorbent that was found. Rubidium carbonate sorbents consistently performed about one half as well in terms of carbon dioxide removed in time. The best performance achieved was that of a 40 percent rubidium carbonate sorbent removing, after 60 minutes of sorption from a 0.3% carbon dioxide stream, 0.046 grams of carbon dioxide per total sorbent weight. The best potassium carbonate sorbent removed 0.105 grams carbon dioxide per total weight after 60 minutes sorption from the same stream.

The results presented in Figure 7 show many of the aspects of gas - consumable solid reactions. First and foremost is the fact of a time decrease of rate, whether an overall rate as in Figure 7 or a flow independent rate as in Figure 9. The time decrease characteristic comes from (1) the fact that the solid reactant is being consumed and less of it is available for reaction as its conversion increases; and (2) the plugging of fine pores in about the solid reactant as the solid product expands during reaction. This can be seen between the 40 and 70 weight percent potassium carbonate sorbents, as the 70 percent sorbent having almost twice as much reactant, shuts down sooner.

The dependence of flowrate is seen for the 40 weight percent sorbent at 0.7 and 7.6 liters per minute at STP. At very low flow rates through the channel the residence time is quite long. Most molecules of carbon dioxide have a good chance to react. The behavior approaches that typically reported for packed bed sorbers as "breakthrough" curves. So here, even though the channel has a large air space (.24cm) above the

# FOLDOUT FRAME



FOLDOUT FRAME

2

FIGURE 7 BEHAVIOR OF SORPTION RATE FOR  
VARIOUS SORBENTS

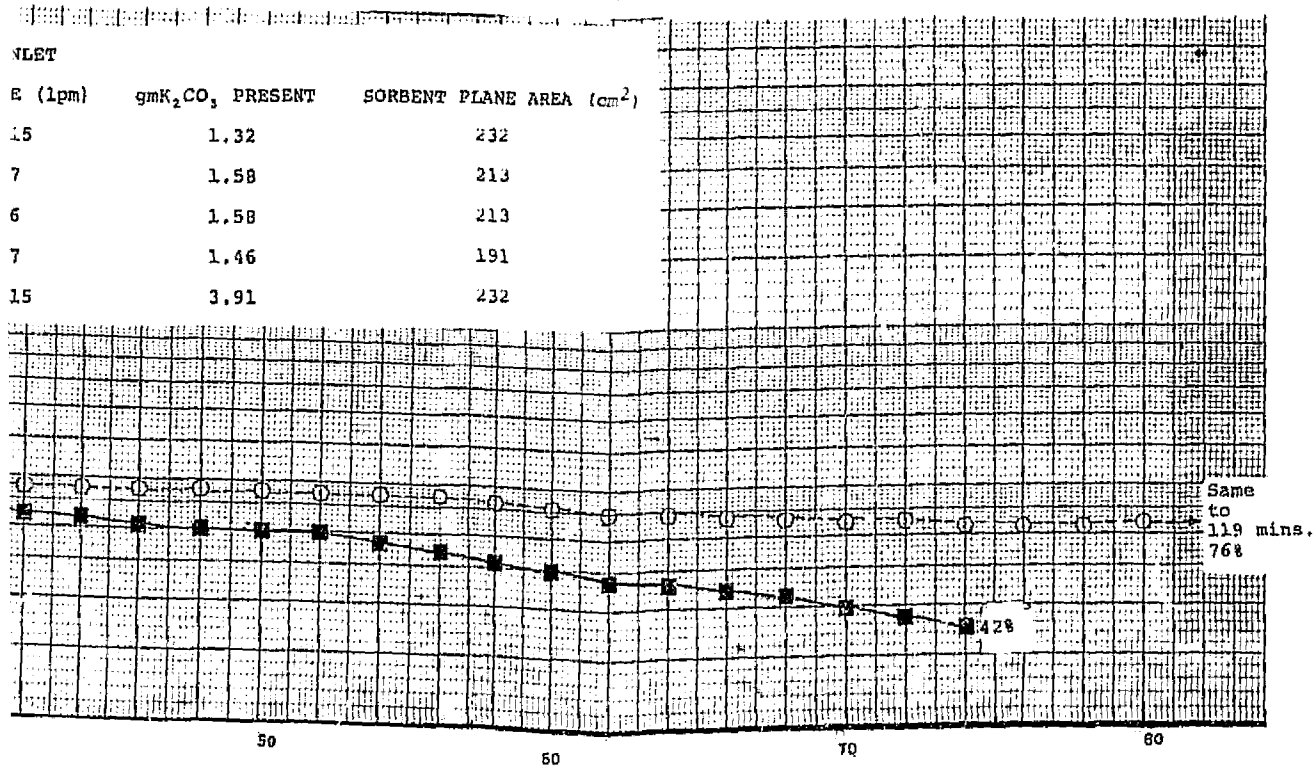
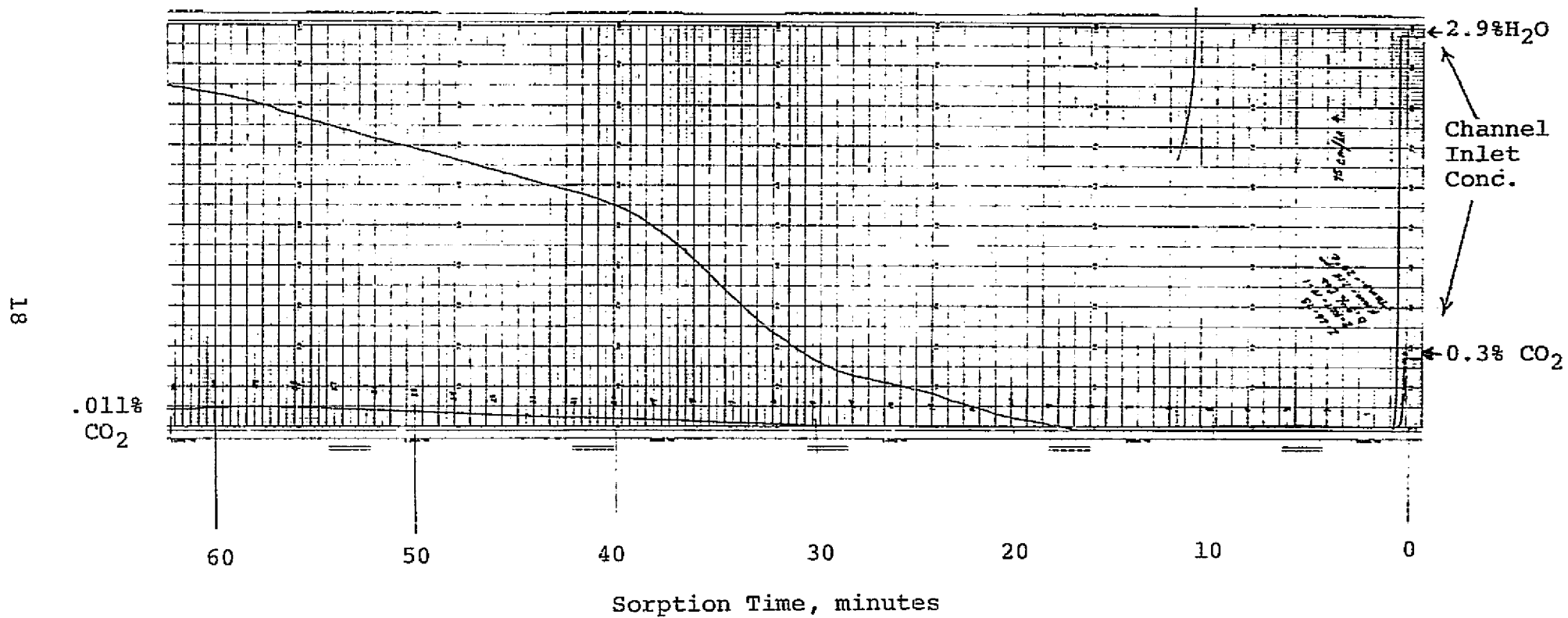


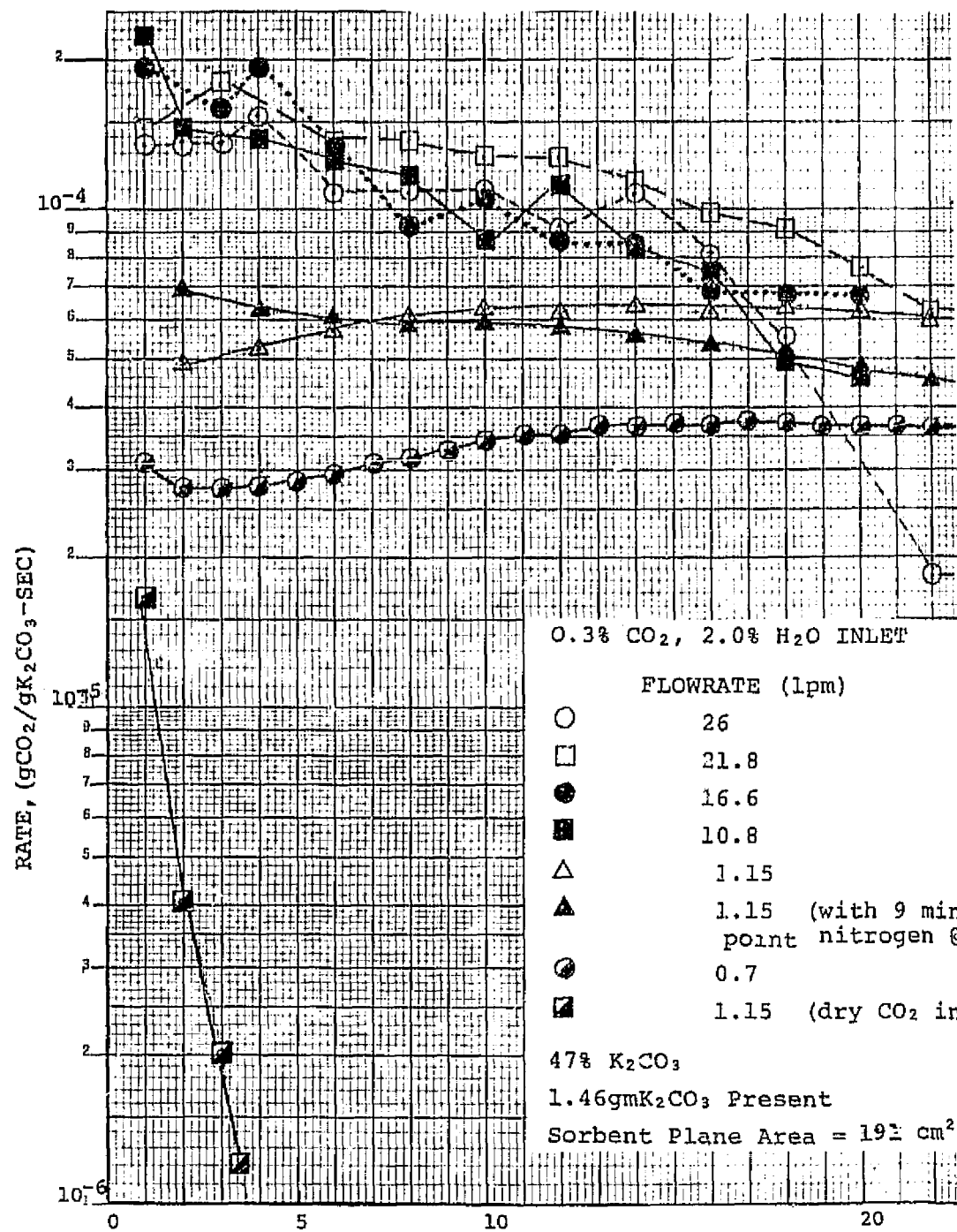
FIGURE 8

ACTUAL RECORDING OUTPUT FROM CHANNEL - RESEMBLES  
CONVENTIONAL PACKED BED "BREAKTHROUGH" CURVES





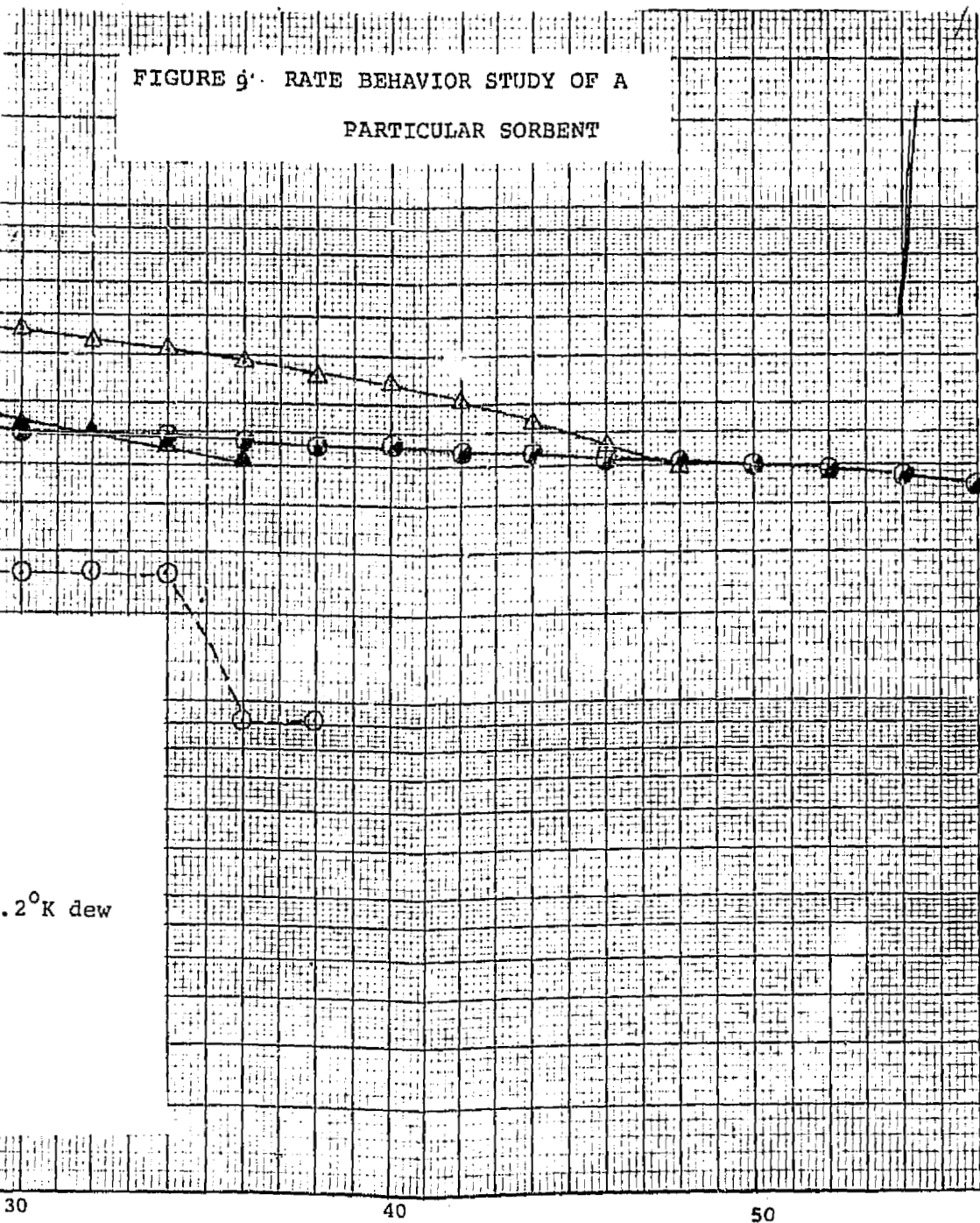
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2

WITHOUT FRAME

FIGURE 9. RATE BEHAVIOR STUDY OF A  
PARTICULAR SORBENT



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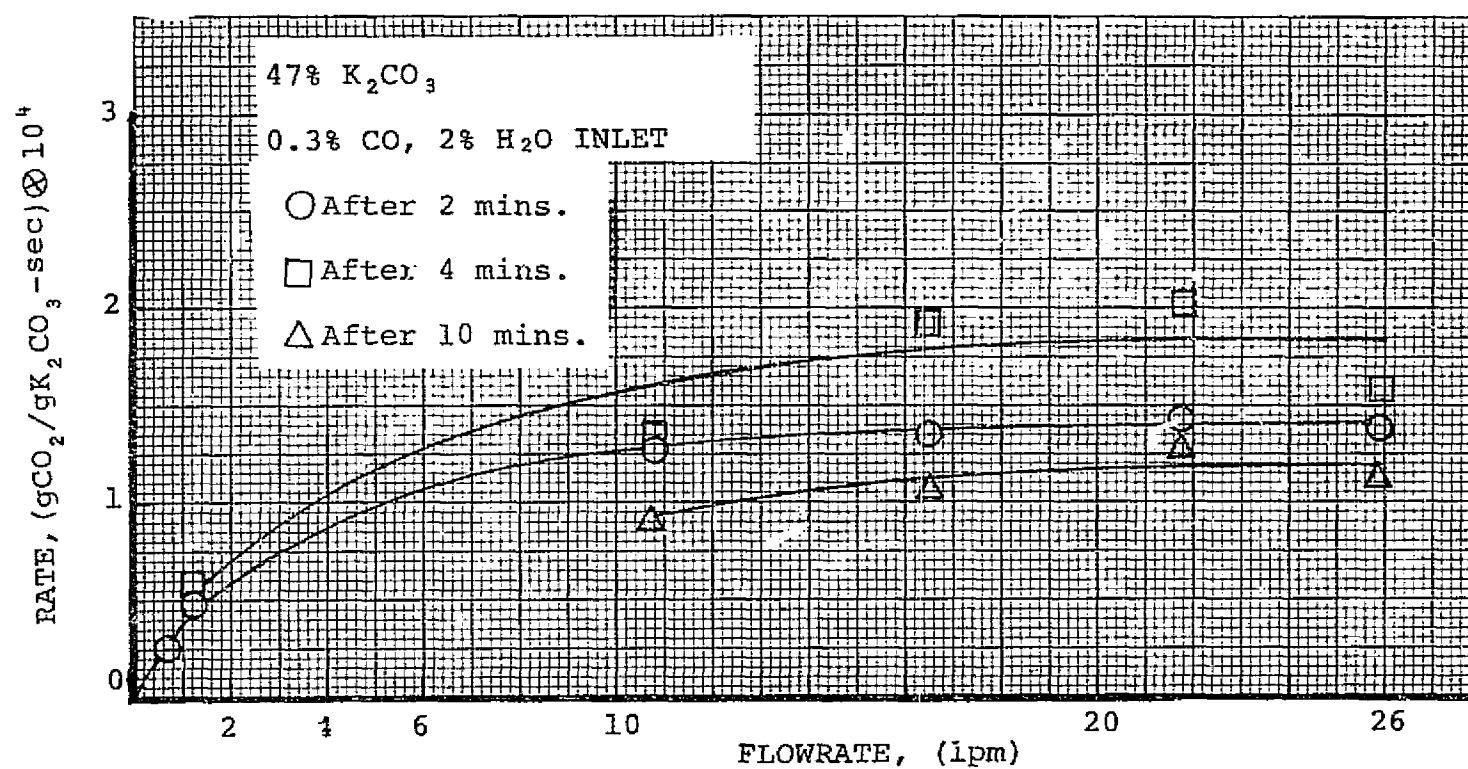
30.5 cm long sorbent layer, the channel does produce breakthrough type curves as is seen in Figure 8, an actual recorder output showing carbon dioxide outlet concentration "breaking-through" after a certain time.

At high flowrates, the diffusional resistance of the carbon dioxide to the sorbent layer is minimized and the conversions obtained represent the "true" or at least a flow independent reaction rate. The flow independent reaction rate is the quantity that will show whether or not a particular carbonate can react fast enough with carbon dioxide in an actual device. For NASA purposes, because of high device capacity this is as fast as the carbon dioxide enters the sorber. The low flowrate conversion data indicative of high residence times in the reactor shows the capacity for carbon dioxide pick-up.

Figure 9 presents a flowrate variation study for one particular sorbent, namely 47 weight percent potassium carbonate. Sorption of carbon dioxide was at room temperature from an inlet stream of 0.3 mole percent carbon dioxide, 2.0 mole percent water in air. An important effect of the simultaneous sorption of water can be seen upon the initial rate behavior. Water is necessary for the reaction with the carbonate as is obviously seen with the dry carbon dioxide stream. For runs, however, with the sorbent initially dry and with wet inlet streams, the sorption rate typically falls slightly until sufficient water is sorbed. The rate then increases for a period and then produces its characteristic time decrease of rate. An additional sorption of water occurs as the result of the hydration of potassium carbonate. This hydrate ( $K_2CO_3 \cdot \frac{3}{2} H_2O$ ) also reacts with carbon dioxide to form the bicarbonate. Presaturating the sorbent partially with wet nitrogen prior to the introduction of carbon dioxide removes this dipping effect in the rate. Slightly higher initial rates are obtained as is shown with the runs represented by the open and closed triangles. However, as expected due to pore volume reduction by the hydrate, the presaturation technique for rate study reduces the rate and conversion in time, and hence capacity. Thus, for a sorbent designed to remove as much carbon dioxide as possible within a certain time, initially dry sorbents are recommended, the latter results as a natural consequence of the regeneration process aboard the base ship in actual EVA missions.

This particular effect of water forces the analysis for the flow independent rate of sorption to be done with the channel using the conventional differential reactor approach. Large errors are introduced into the integral equation analysis at the initial times where the different amounts of water present in the sorbent produce poorly defined rates. More water is picked up by the sorbent as the flowrate increases. The rates obtained at and above a certain high flowrate would be flow independent, as is indicated in Figure 10 by the constancy of rate values at various sorption times.

FIGURE 10 ACHIEVEMENT OF FLOW INDEPENDENT  
RATE



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The total amount of water sorbed does not exceed the stoichiometric amount required for reaction plus hydration, henceforth the sorbents would not dry out a recirculating atmosphere to any detrimental effect.

### 7.2 Regeneration of Sorbent - Bicarbonate Back to Carbonate

After each sorption run the sorbent sheets were regenerated in place in the channel by heating the channel to 411°K with nitrogen or air flowing through. The channel air flowrate during regeneration is not directly related to regeneration, as the sorbent could be regenerated with no air using vacuum and/or heat. The regeneration flowrate was chosen as that which produced a channel outlet carbon dioxide concentration within the infrared analyzer's best measurement range. Figure 11 shows a typical recorder chart outlet concentration record of regenerated carbon dioxide and water vapor.

The thermal regeneration of sorbent sheet is complete as was found by approximate mass balance checks between carbon dioxide sorbed and carbon dioxide regenerated. To confirm this, identical rates and conversion (within experiment error) were found after ten cycles as shown in Figure 12. A cycle consists of sorption of carbon dioxide at room temperature followed by heating to drive off the carbon dioxide and water, then cooling down to room temperature to start another sorption. The cycling ability or structural integrity of the sorbent in this initial test is excellent. Potentially, a long sorbent life is expected as is shown later.

Regeneration of the sorbent is also possible using vacuum only. Theoretically a vacuum of approximately 100 microns is sufficient to reverse the reaction, or decompose the bicarbonate. These vacuum conditions are readily available in space.

Although beyond the original scope of the project some vacuum regeneration was explored.

A sorbent sheet was regenerated in this manner using a laboratory vacuum pump. The sorbent sheet was reacted in the channel and thermally regenerated as normal for several runs to establish its performance. Then it was removed from the channel and placed in a vacuum flask. After approximately 45 minutes the vacuum as measured with a electronic vacuum gauge was down to 50 microns. This sheet was then quickly placed back in the channel and heated to see if any carbon dioxide was driven off. Only slight traces of carbon dioxide were sensed by the Lira infrared analyzer.

This procedure was necessary as attempts to draw a vacuum on the channel apparatus were not successful. During the vacuum

FIGURE 11 TYPICAL THERMAL REGENERATION  
CHART RECORD

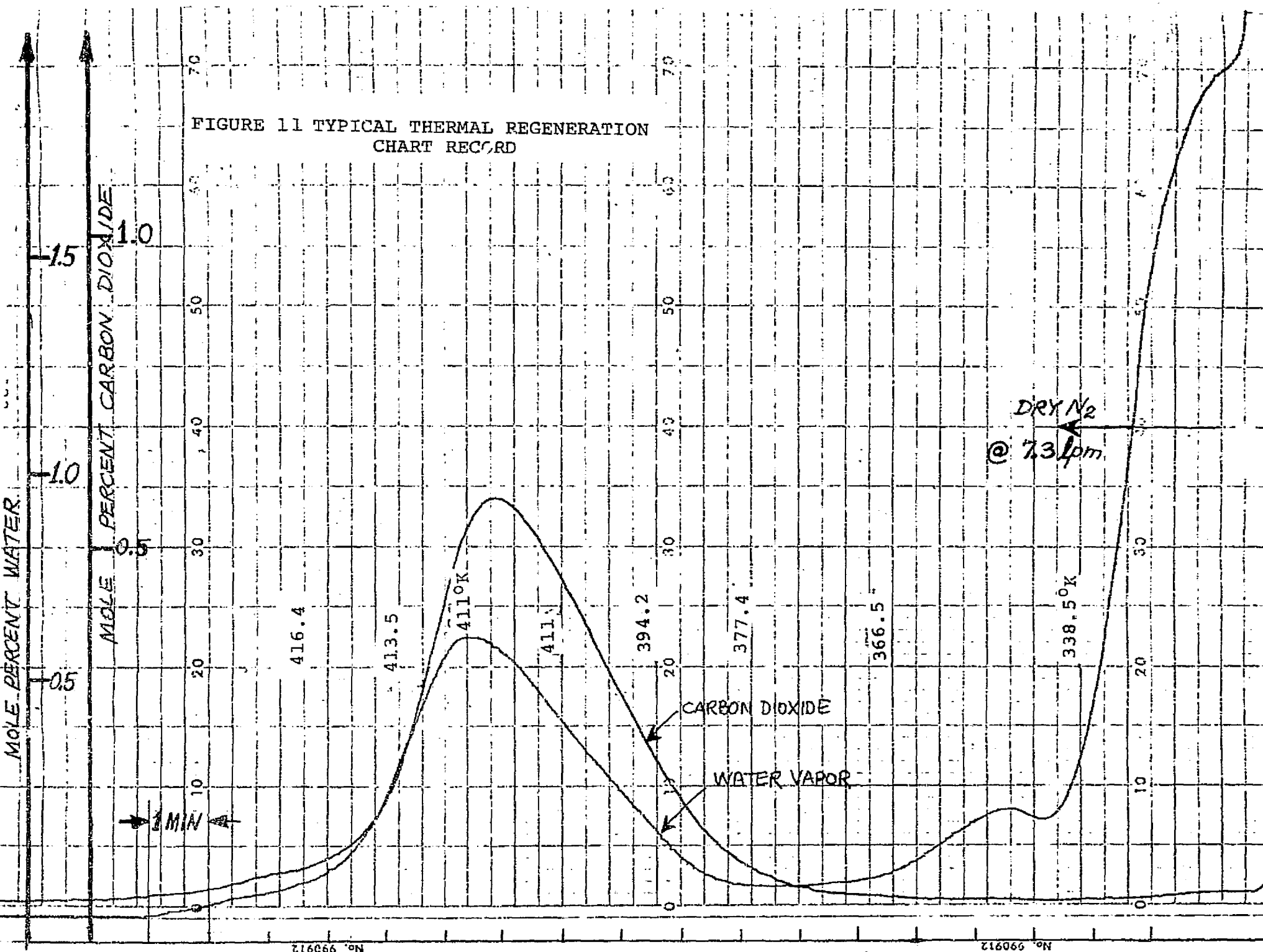
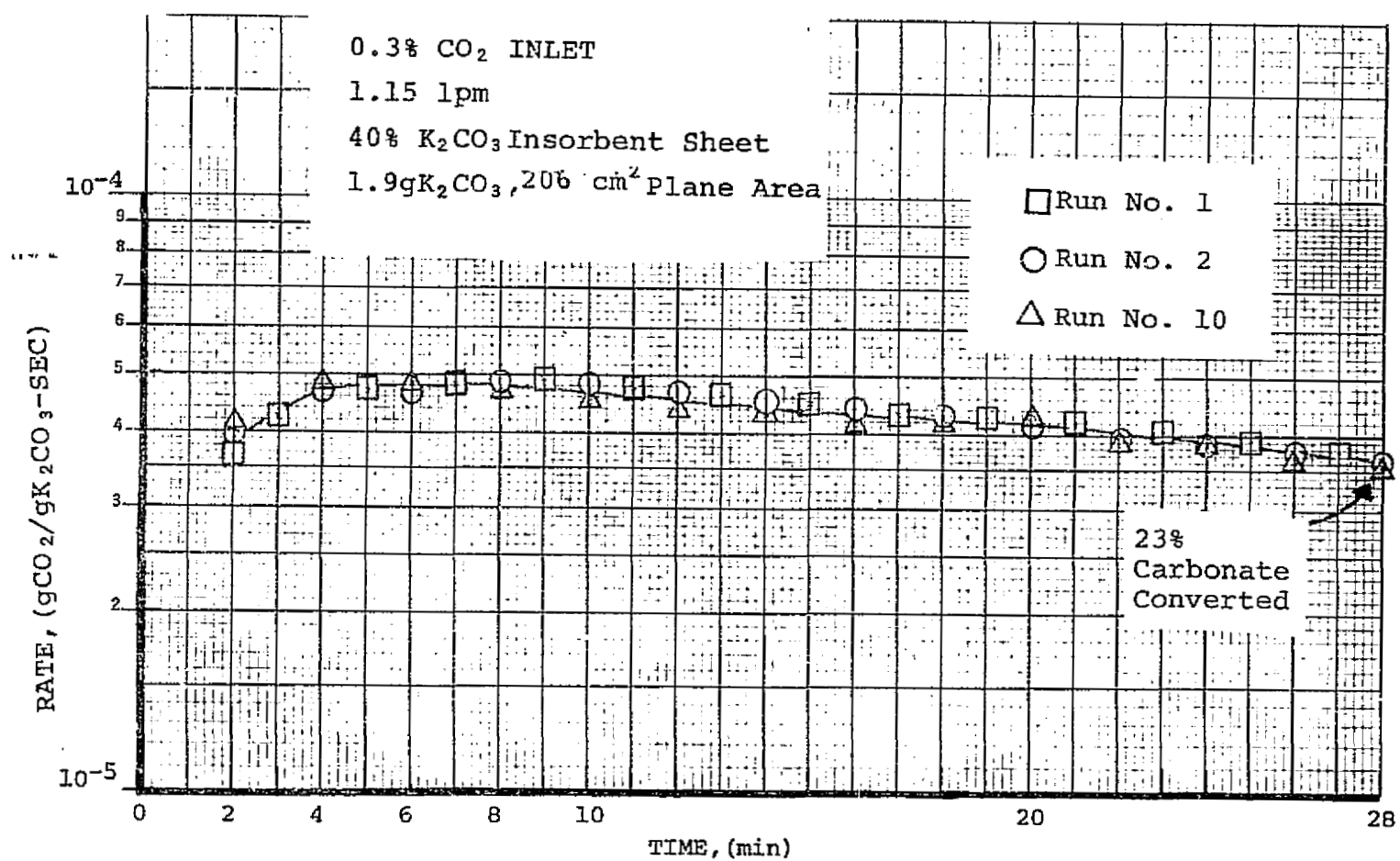


FIGURE 12 SORBENT PERFORMANCE DURING  
CYCLE TEST

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application to the flask, syringe samples of gas from the flask were fed to a gas chromatograph. The chromatograph did show less carbon dioxide present towards the end of the test than the beginning, but due to leaks to the syringe or chromatograph, a constant oxygen peak was measured. Hence the chromatograph evidence is at least qualitative. Vacuum regeneration seems entirely possible. No facts are present that deny regeneration by vacuum in at least the same magnitude of time as that by thermal regeneration.

An additional regeneration scheme possible could be to use a little bit of heat in combination with vacuum to economize time and rapidly remove the carbon dioxide from the system.

Vacuum regeneration is of interest since it permits smaller units to be designed which can be regenerated in situ during the EVA mission. Further vacuum regeneration, even at the base ship would require far less power consumption. The system becomes attractive for more than just EVA missions and could be considered as the primary carbon dioxide removal system in the base ship itself.

### 7.3 Optimization of Potassium Carbonate Sorbent Composition

After the initial investigation of sorption characteristics the study was directed at investigation of carbon dioxide sorbent sheets in terms of the weight ratio of alkali metal carbonate to inactive support material and binder. In review, for the NASA mission, the optimum sorbent sheet should remove the largest amount of carbon dioxide for the least total sorbent weight. A large number of different sorbent compositions were tested according to this criteria. The results are presented in Figure 13 which shows the grams of carbon dioxide removed per total sorbent weight plotted against the grams of alkali metal carbonate present or roughly, the weight percent of carbonate in the sorbent. Note that the ordinate is grams of total sorbent not just the grams of carbonate present.

All sorption runs in Figure 13 were made in the channel apparatus with an inlet carbon dioxide concentration of 0.3 mole percent flowing at 1.15 lpm at room temperature of 299.1°K. This low flow is in the range of actual flows between sorbent layers of a practical device. The size of each sorbent sheet was 7.6 cm by 31 cm by 0.038 cm thick.

The data plotted in Figure 13 are those obtained after 60 minutes of sorption and chosen as a realistic comparison point. Sorption of carbon dioxide still continues beyond this time. Hence the figure does not show the maximum carbon dioxide pick-up that could be obtained. For the purposes of this NASA program, the 60 minute mark for reporting sorption data was chosen because of the fact that up to 60 minutes at least, the



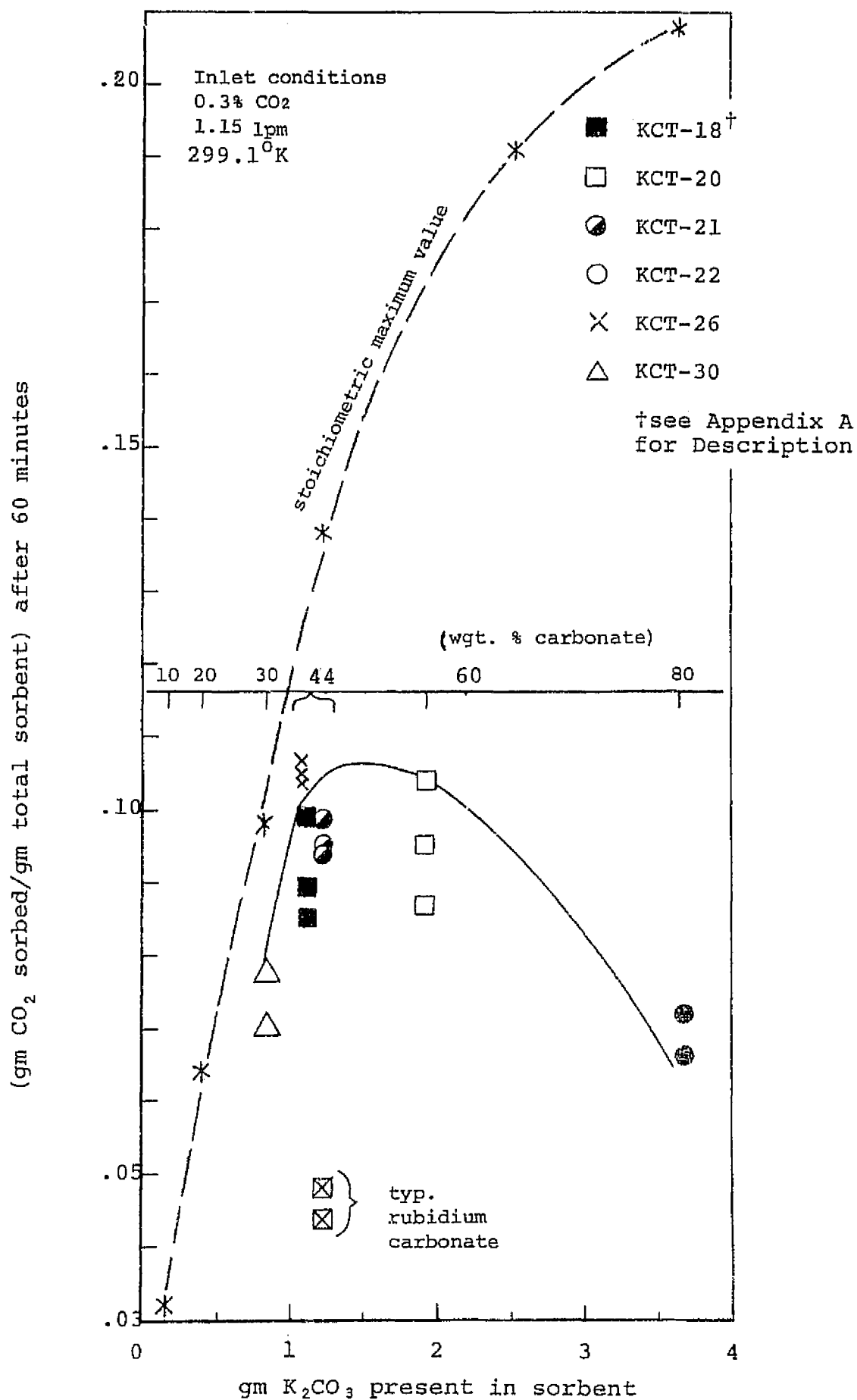


FIGURE 13 PERFORMANCE OF VARIOUS  
COMPOSITION SORBENTS

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outlet concentration of carbon dioxide was always below 0.1 mole percent. Typical outlet concentration behavior is presented in Figure 8 showing the actual outlet concentrations of carbon dioxide and water from the channel sorber apparatus at flow conditions simulating actual operating conditions. The inlet concentration of carbon dioxide and water are 0.3% and 2.0%, respectively. The flowrate is 1.15 lpm at 299.1°K. This actual output for a single sorbent sheet in the apparatus closely resembles the commonly resported "breakthrough" curves for packed bed sorbers. Decreasing the flowrate and the channel gas space above the sorbent would produce a "sharper" knee in the breakthrough curve and maintain the outlet carbon dioxide concentration lower for a longer time. The 1.15 lpm flowrate is used primarily in this study as a base value for comparing various sorbent performances but as mentioned, it is close to representing actual flows inbetween sheets in an actual device. Note that at the 60 minute reporting mark, the outlet concentration is just approaching 0.1% CO<sub>2</sub>.

The data points in Figure 13 show the performance of the various composition sorbents and indicate an optimum sorbent composition at about 44 weight percent potassium carbonate. Many other sorbent preparations about 44 percent were tested but not reported because of significantly reduced sorption of carbon dioxide. Porosimeter tests indicated that some of these did not have sufficient void volumes. Some of these sorbents contained various small additions of graphite or carbon black with the intent of strengthening the macropore structure. However, all that the additional inert material did was to fill up voids within the sheets. Hence, minimum components in the sheet permits maximum performance.

Additional test runs with rubidium carbonate sorbents near the optimal potassium carbonate sorbent sheets produced higher outlet concentrations of carbon dioxide during all corresponding times of sorption. The higher regeneration temperature for rubidium carbonate near 473°K compared to 423°K for potassium carbonate along with its higher cost makes rubidium carbonate a poor candidate for carbon dioxide removal in this manner.

The best of 44% potassium carbonate sorbents, referring to Figure 13, shows 0.105 grams of carbon dioxide sorbed per gram of total sorbent sheet after 60 minutes of sorption. This corresponds to 75% conversion of the potassium carbonate in that sorbent sheet. Differences between the 44% potassium carbonate sorbents in Figure 13 represents slightly different techniques of preparation and various inert additions. The comparison of the actual amounts of carbon dioxide sorbed to the "stoichiometric amount per total sorbent sheet weight" is shown by the dotted curve. The divergence of sorbents with greater than 44% carbonate from this dotted curve is dramatic yet expected considering the pore plugging situation that exists during reaction. Most of the carbonate in the higher composition sheets is

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rendered useless. Evidence supporting this is shown in Figure 14 with porosimeter measurements of average pore radius in Angstroms for the 80% potassium carbonate sorbent in Figure 13. The pore radius distribution before any runs is typical of all sorbents, however, after only two sorption - thermal regeneration cycles, the 80% carbonate sorbent's pore radius distribution shows a marked change to larger pores. This means the small pores initially present have disappeared, or in other words, have been plugged, choking off the gas accessibility to the carbonate beyond.

Sorbents with less than 80% carbonate loading do not exhibit such drastic changes as shown by 44% carbonate sorbent after five cycles. The investigation of cycle life is discussed later. The results for the 44% sorbent in Figure 14 does not represent the best 44% carbonate sorbent. For all sorbents in the optimization study testing was stopped after 5 cycles because of lab time priority to identify optimum sorbents.

### 7.4 Cycle Life of Optimum Sorbent

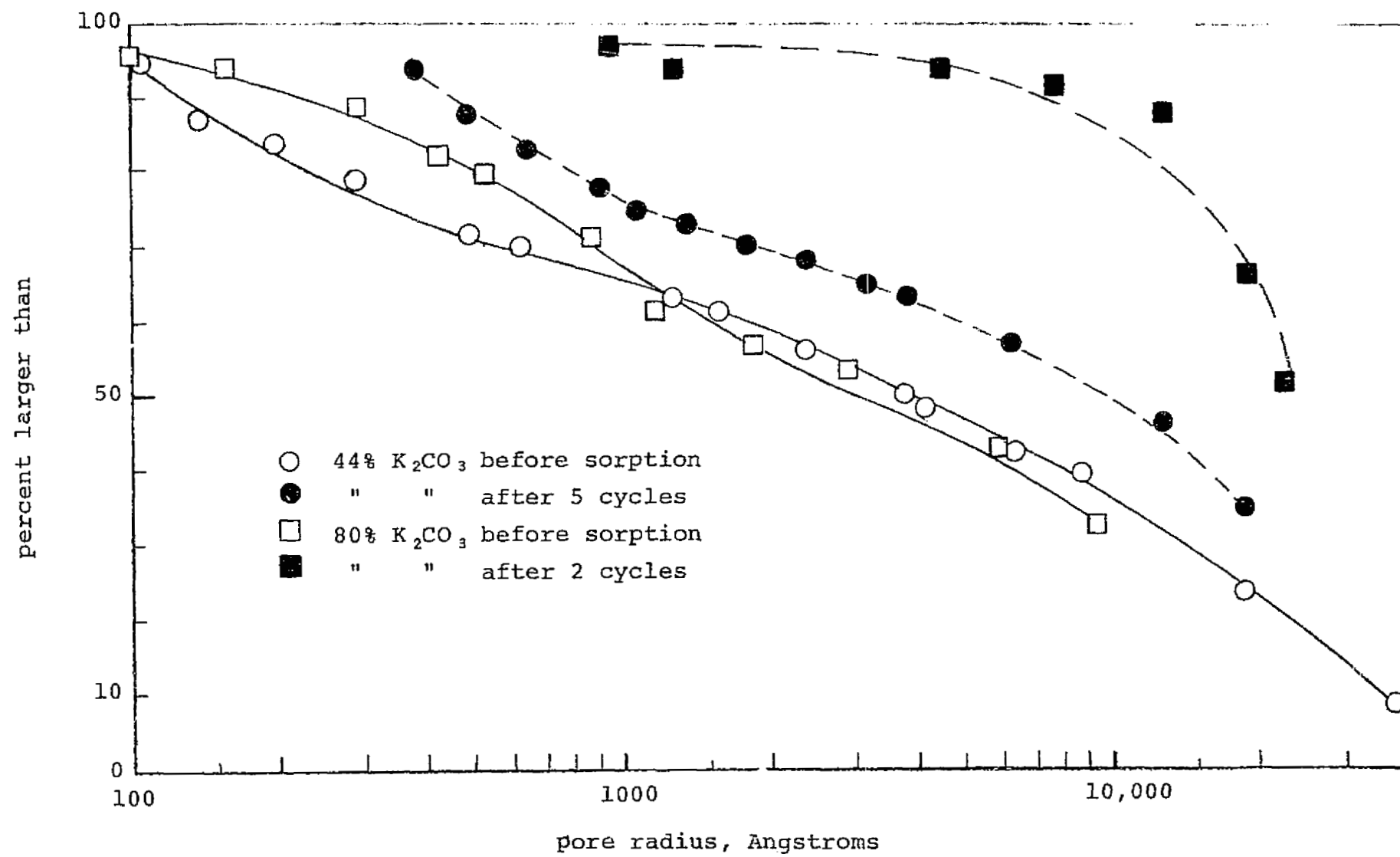
The NASA mission demands a device that can be repeatedly regenerated and reused. Any sorbent system of value has to have a reasonably long cycle life. The sorbent composition that was optimized with respect to maximum removal of carbon dioxide per total weight of sorbent must also demonstrate extended cycling ability.

A cycling test was set-up with the channel apparatus. A multiple switching 24 hour timer was installed to automatically operate solenoid valves for controlling carbon dioxide sorption gas and regeneration air flows as well as the recorder chart, the heaters, and the cooling fan as appropriate.

To proceed with a meaningful cycle test within a reasonable calendar time, six complete cycles per day evolved. A cycle consists of (1) sorption of carbon dioxide from 0.3 mole percent carbon dioxide stream at room temperature of 299.1°K, flowing at 1.15 liters per minute, for 32 minutes; (2) thermal regeneration with air at 3.2 liters per minute requiring 58 minutes; and (3) cooling with room air for 150 minutes before sorption begins again.

The Lira infrared analyzer was recalibrated every morning. It did not wander about significantly overnight or over weekends. A slight variation between night and day was observed. The magnitude of this variation (  $\pm 10\%$  ) considered over the entire cycle life is not significant, in fact that situation could be considered a tougher test for cycle ability.

FIGURE 14 PORE SIZE DISTRIBUTION



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The fraction of potassium carbonate converted per cycle is shown in Figure 15 plotted against the number of the cycle. The fraction converted is approximately constant for 52 cycles at least. The sorbent in this test was the near optimum composition of 44 weight percent potassium carbonate. Figure 15 shows that 30 to 35 percent of the carbonate was consistently converted in each cycle. This conversion level was dictated by including a reasonable number of cycles per day. Allowing the sorption to proceed for 60 - 70 minutes or 75% conversion for example would allow at most four cycles per day mainly because of channel cooling time.

The sorbent performed excellently in this test. A slight dimensional shrinkage of about 10% was seen in the sorbent layer after 70 cycles. The pore size distribution for this sorbent before and after cycling was determined and is presented in Figure 6. As can be seen, after 70 cycles the number of small pores have been significantly reduced showing the probable reason for the reduced conversion at the cycling end.

To further improve the cycle life it is necessary to investigate the subtle aspects of the physical support and dispersion of reactive particles. The dimensional shrinkage could be caused by the non-optimum level of the polytetrafluoroethylene binder. For example, a possible improvement would be to press the sorbent layer on some grid that could be rigid enough to hold the form of channel-type gas spaces between sheets.

# FOLDOUT FRAME

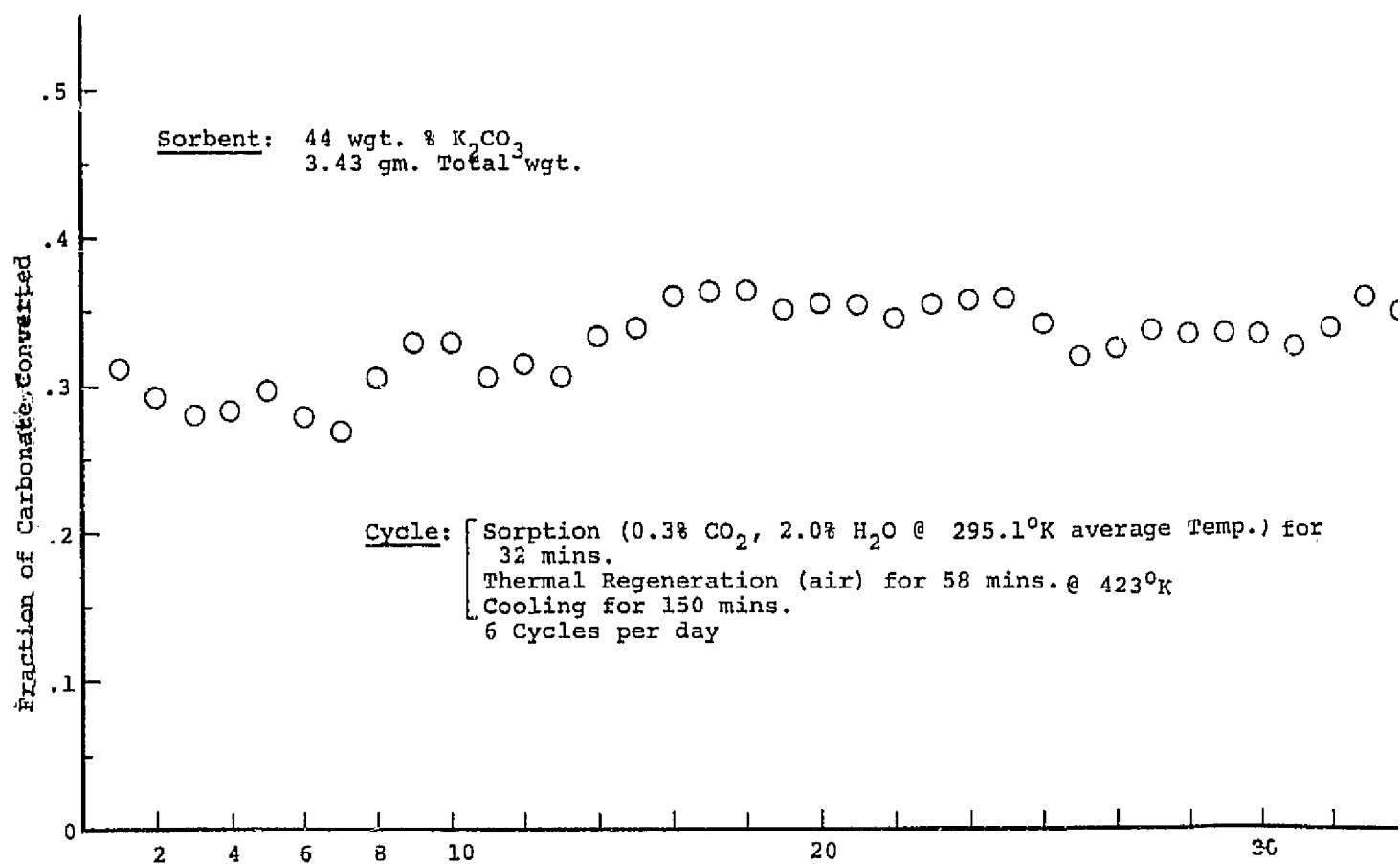
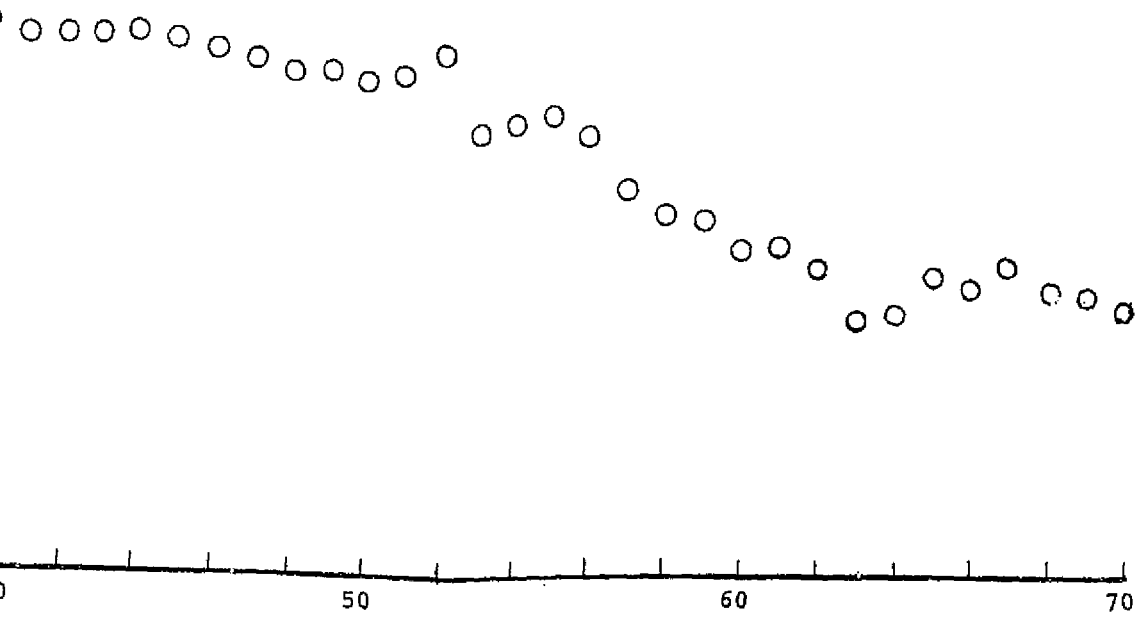


Figure 15 Cycle Life of Optimum Sorbent

FOLDOUT FRAME 2



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### 8.0 SORBER DESIGN FROM EXPERIMENTAL DATA

The carbon dioxide sorption data from the flowing channel sorber apparatus can be used for the design of two different types of carbon dioxide sorbers.

One type of sorbing/regenerating or mass exchanging device operates by continuously sorbing and regenerating in short cycles such as the "Munters" rotating wheel air conditioner.(9) The sorption time or contact time in this device is small (on the order of a few seconds to minutes). Hence, to design the smallest, most efficient sorber requires knowing the maximum possible or flow independent rate of reaction. Such a rate value from Figure 9, for example would be the value at the highest flowrates and taken near the one or two minute mark of sorption. Since devices of this type sorb for only short times before regeneration occurs, maximizing the amount of carbon dioxide removed per sorbent weight is not involved in this design. This sorber design could be designated as rate controlled. It would be the type of sorber to use for continuous duty aboard the base ship.

The other basic type of sorber corresponds with the EVA program's goals. This sorber is a batch-regenerable device where the operating principle is to react as much carbon dioxide as is possible over a long (several hours) period of time.

The design information for this sorber can be interpreted in either of two equivalent ways. One way is to use the rate of conversion data from Figures 7 and 9, that is those quite constant values at the lowest flowrates. Strictly speaking these values are not reaction rates but flow dependent conversion information for that particular sorbent in that particular channel at that particular flowrate. The numbers are useful for the design of a full scale unit by visualizing the building of that unit by the stacking of many channel units, each of which performs as the individual channel represented in Figures 7 and 9.

The other equivalent design procedure considers the total carbon dioxide removed by one sheet in the channel in the time that the outlet concentration of carbon dioxide remains at zero or some specified level. This is equivalent to the "rate" method because it represents the integral of that quantity. Coupled with the low outlet concentration this carbon dioxide removed number represents a simple yet realistic design number. A rough design estimate is given in this way for the near optimum sorbent.



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The total sorbent weight for an 8 hour EVA mission exclusive of physical containment weight for each of the sorbent in Figure 13 is plotted in Figure 16. A carbon dioxide removal duty of 72 grams per hour per man was used with the actual sorbent performance to calculate the total weight of sorbent sheets required. Figure 16 presents a minimum weight of 5.5Kg for the 44% potassium carbonate sorbent required for the mission.

A possible arrangement of the sorbent sheets in the sorber for the 8 hour EVA mission is shown in Figure 17A. Simple stacking of 0.114 cm sorbent sheets with 0.038 cm gas flow spaces yields the unit design. The thickness of the sorbent sheet is taken more than double its channel predecessor because carbon dioxide will contact the sheet from both sides. Likewise for efficient space packing of the sorbent, sheets of .0% porosity are chosen rather than the 92% porosity.

This unit has been conservatively estimated first with the stiff duty of 72 grams carbon dioxide per hour for 8 hours, and secondly, the data used in the design is based on only 75% conversion of potassium carbonate in the sorbent. Indeed more carbonate will be converted near the entrance section of the sorber than in the exit section. If one half of the sorbent goes to 95% conversion then the unit can pick up 10% more carbon dioxide than the 576g carbon dioxide duty.

The data of this study is useful for rough sizing sorber units and it shows reasonable units, however information on actual configuration units is necessary to avoid over design precautions.

For example, a different stacking geometry could reduce the volume or distribute it in other ways. A spirally wound sorbent or a series of spirally wound sorbent cans are possible candidates.

With the possibility of in place vacuum regeneration of the sorber unit, the size can be easily reduced to 1/4 of the full size unit. For example, if one half of the unit is sorbing for one hour while the other half is regenerating, then the overall sorber would be only 1/4 of the full size unit as seen in Figure 17B.

The fact that the sorption of carbon dioxide required the simultaneously sorption of approximately equimolar amounts of water can be a useful feature considering the overall environmental control system. The sorbents remove water on the order of 0.5 gram per 4 grams of sorbent weight. This amount is the amount of water needed for the hydration of the carbonate and for the reaction of the carbonate to the bicarbonate. The sorbents do not remove anymore water than this and would not dry out the environment.

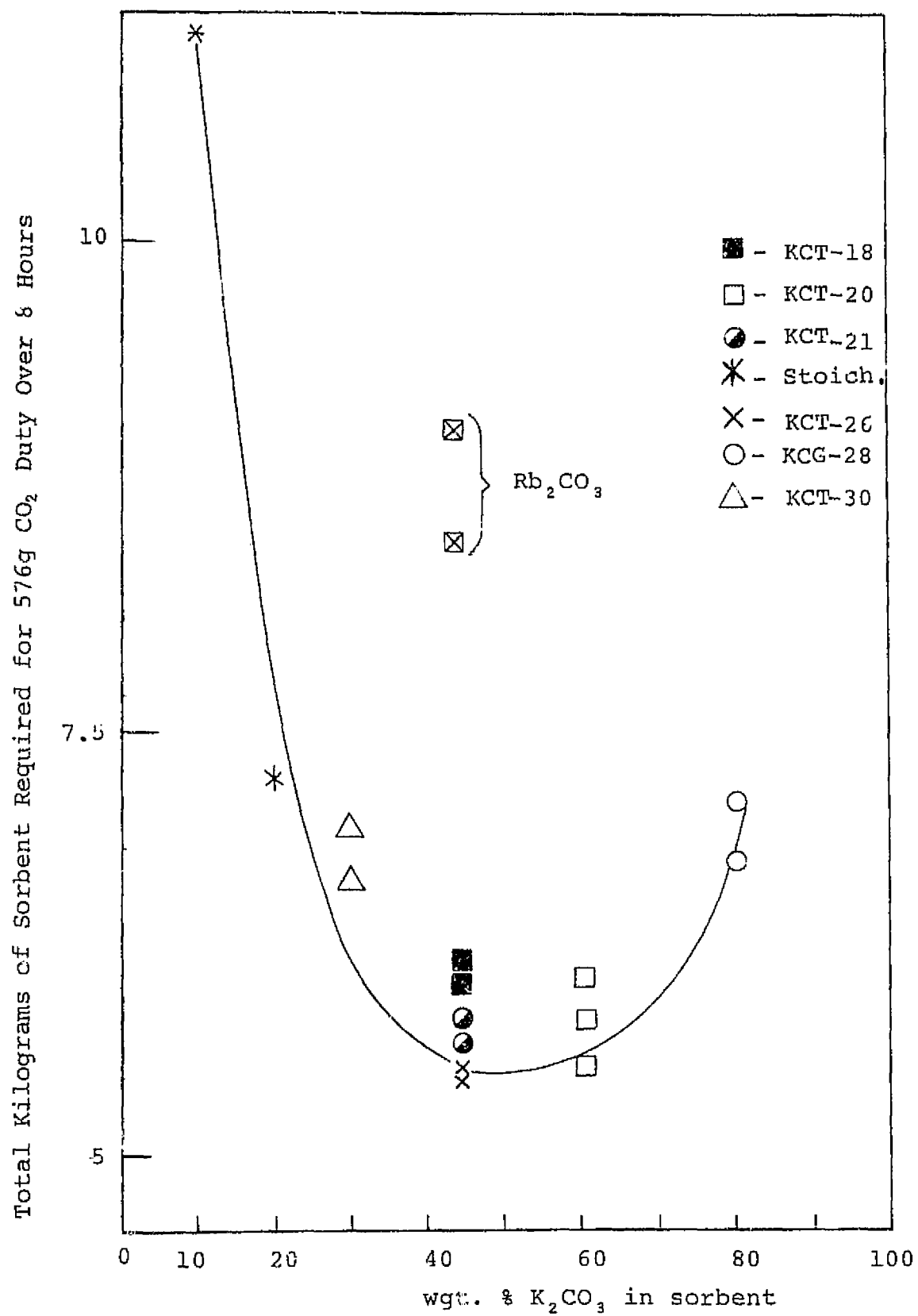
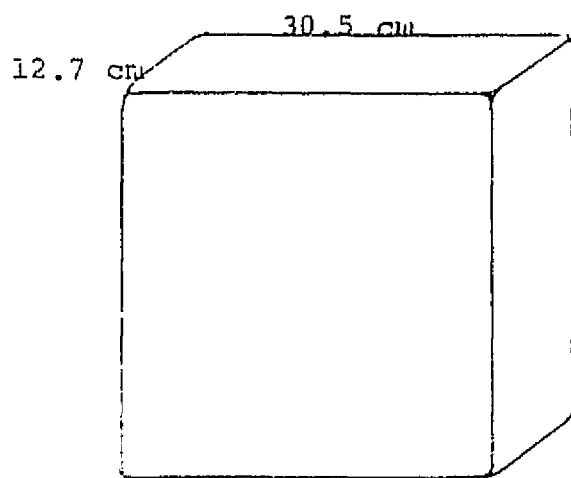
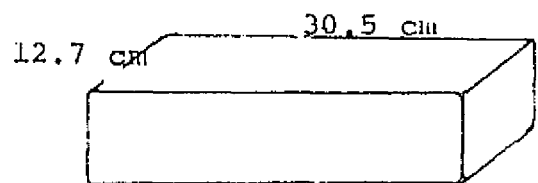


FIGURE 16 TOTAL SORBENT WEIGHT REQUIRED FOR MISSION



Regenerable CO<sub>2</sub> Sorber  
 8 Hour Continuous Duty Unit  
 (72g CO<sub>2</sub>/hour)  
 Volume: 13.8l

FIGURE 17A 8 Hour Continuous Sorber



Vacuum Regenerable CO<sub>2</sub> Sorber  
 (1 Hour Sorption for half of  
 unit while other half re-  
 generates)  
 Volume: 3.95l

FIGURE 17B One Quarter Size Vacuum Regenerable Sorber

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With this feature, the load upon the present water control system could be lessened and hence the size and weight of that unit could be reduced.

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9.0 RECOMMENDATIONS

1. A full size one man, 8 hour mission thermally regenerative EVA unit should be built and evaluated based on the present system.

2. A full size one man, 8 hour mission, vacuum regenerative EVA unit should be built and evaluated based on the present system.

3. Performance of the above two units should be compared

4. A design study should be made to evaluate a vacuum regenerative unit for simultaneous moisture and carbon dioxide control within one system.

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10.0 CONCLUSIONS

1. The potassium carbonate-bicarbonate chemistry is effective for maintaining low carbon dioxide atmosphere in air streams.

2. The chemical can be effectively distributed and supported in sheet form using silica-polytetrafluorethylene carbonate composite.

3. Sheets of the above material can be continuously, reproducibly and in-expensively manufactured.

4. These materials can maintain the carbon dioxide level below 0.1% for periods required in EVA missions.

5. Repetitive thermal regeneration at 423°K without significant loss in capacity was demonstrated for 50 cycles.

6. Preliminary data suggest vacuum regeneration at ambient temperature is also feasible.

7. A compact, less than 14 liters unit would be required to remove the carbon dioxide expelled by a hard working man (72gm/hour) for an 8 hour period.

8. An even more compact, less than 4 liter unit could be built for cycle vacuum regeneration on a one hour cycle for the same mission. Considerably less experimental data is available at present to support this conclusion.

9. A dual carbon dioxide-water removal role can be performed by the carbonate-bicarbonate system thereby considerably reducing the moisture control problem.

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APPENDIX A

DESCRIPTION OF SORBENTS

Sorbent	Composition (weight Per Cent)				Preparation Comments
	Carbonate	Support	Silica Gel	Binder	
KCT-18	44	49.8		5.2	0.96% carbon black
KCT-20	60	36.2		3.8	
KCT-21	44	50.2		5.8	
KCT-22	80	18.1		1.9	
KCT-26	44	45.4		10.6	1.05% graphite 1% graphite
KCT-28	44	44.5		10.5	
KCT-30	30	55.8		13.2	

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APPENDIX B

THERMODYNAMIC EQUILIBRIUM FOR ALKALI  
METAL CARBONATE-BICARBONATE REACTIONS

Thermodynamic Functions for the Alkali  
Carbonate-Bicarbonate System

M	$\Delta G^\circ_{298^\circ K}$	$\Delta H^\circ_{298^\circ K}$
Li	-1.45 KCal/g-mole	-11.61 KCal/g-mole
Na	-7.11 " "	-30.85 " "
K	-8.11 " "	-32.82 " "
Rb	-10.11 " "	-35.55 " "
Cs	-13.11 " "	-37.55 " "

$$\text{Li: } \log_{10} K_p = \frac{2419}{T} - 0.684 \log_{10} T - 0.32 \times 10^{-3} T - 5.288$$

$$\text{Na: } \log_{10} K_p = \frac{6151}{T} - 5.355 \log_{10} T + 1.105 \times 10^{-3} T - 2.557$$

$$\text{K: } \log_{10} K_p = \frac{6593}{T} - 4.26 \log_{10} T - 0.32 \times 10^{-3} T - 5.551$$

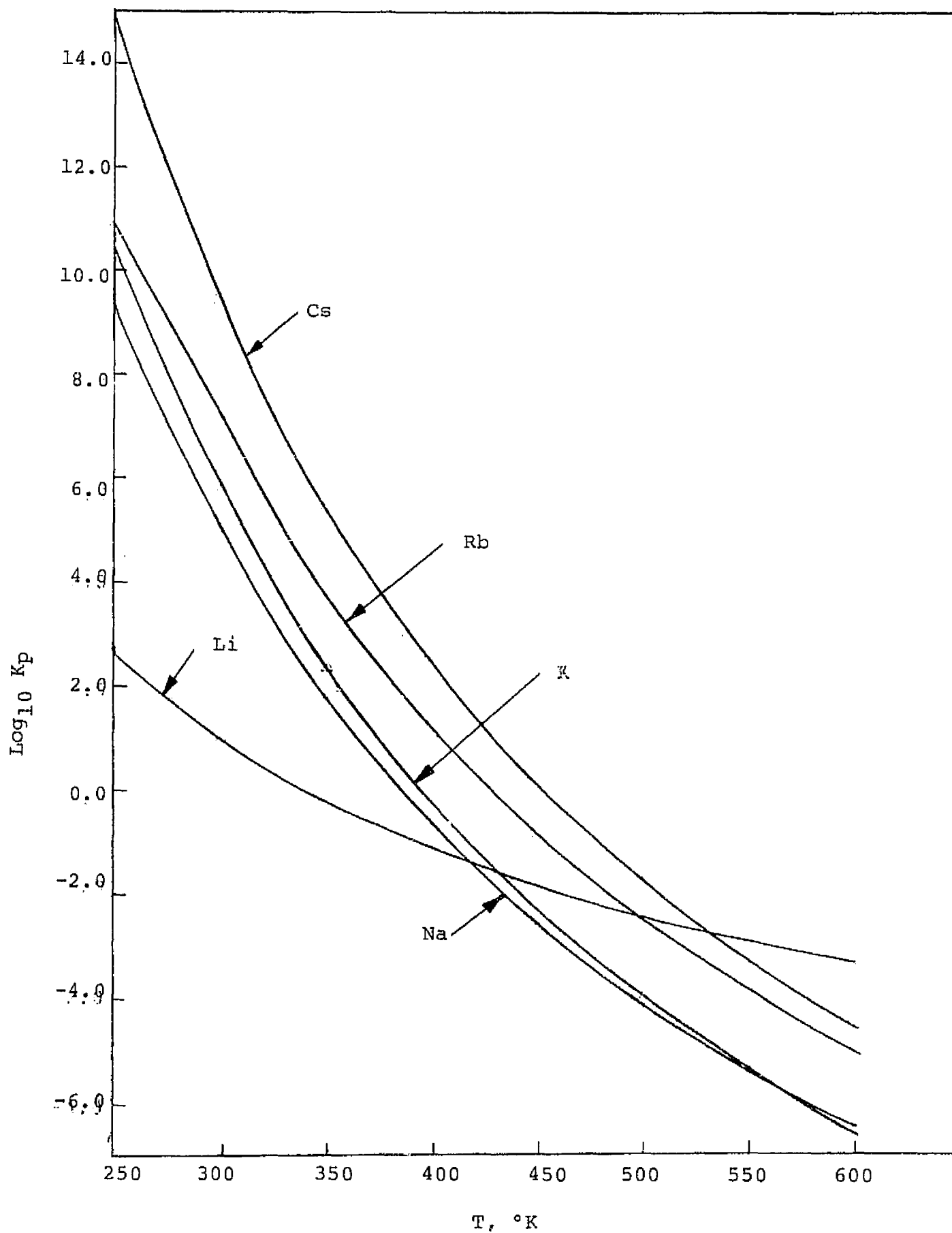
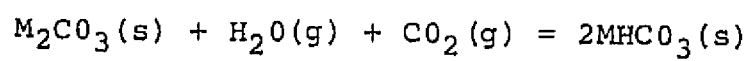
$$\text{Rb: } \log_{10} K_p = \frac{6691}{T} - 3.50 \log_{10} T - 0.32 \times 10^{-3} T - 6.270$$

$$\text{Cs: } \log_{10} K_p = \frac{7725}{T} - 3.50 \log_{10} T - 0.32 \times 10^{-3} T - 7.538$$

$$\text{Where: } \log_{10} K_p = \log_{10} \frac{1}{(p_{\text{CO}_2}) (p_{\text{H}_2\text{O}})} = \log_{10} \frac{1}{(p_{\text{CO}_2})^2} = -2 \log p_{\text{CO}_2}$$

$$\text{Total pressure} = p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 2p_{\text{CO}_2}$$





EQUILIBRIUM DATA FOR VARIOUS METAL CARBONATE SALTS

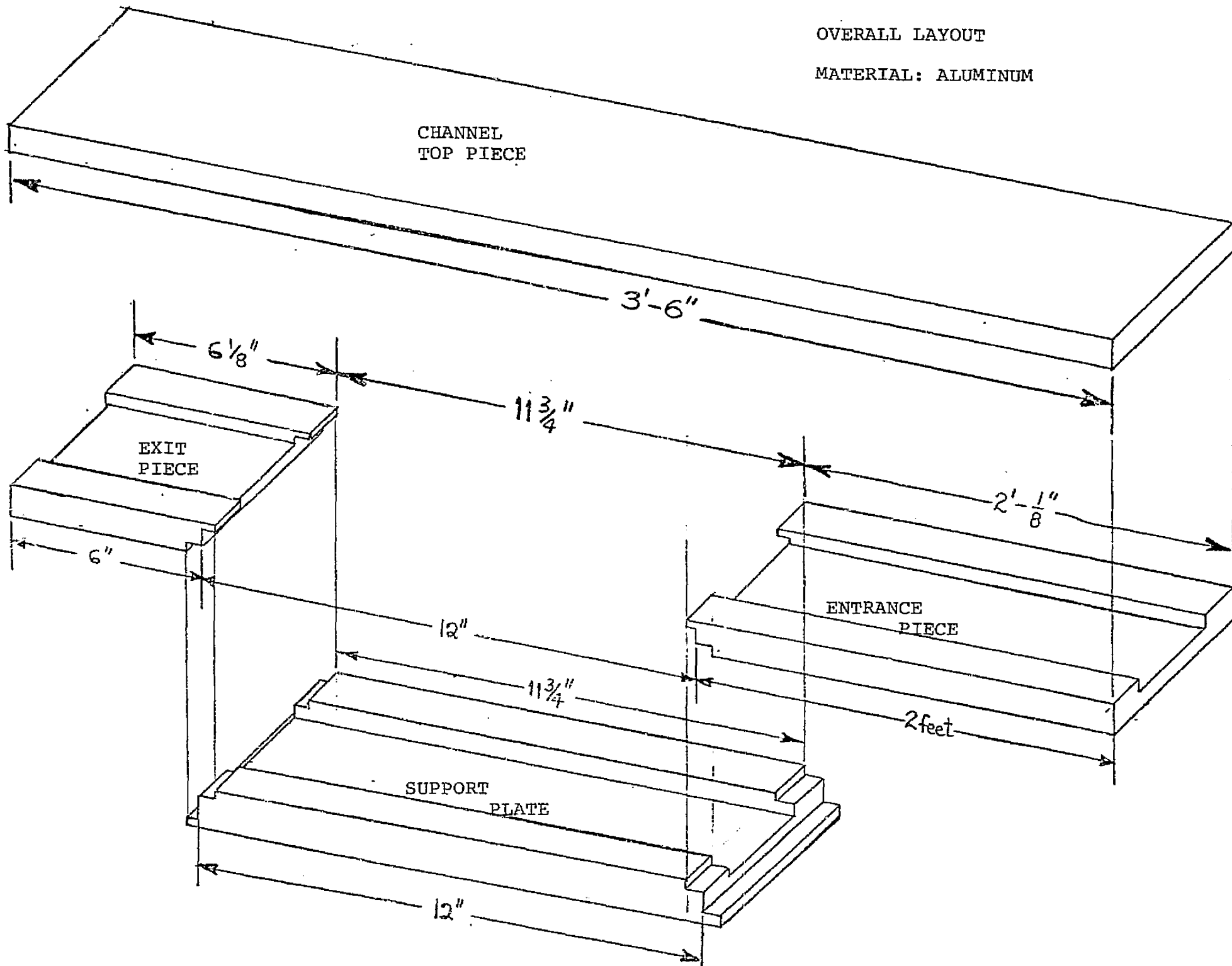
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APPENDIX C

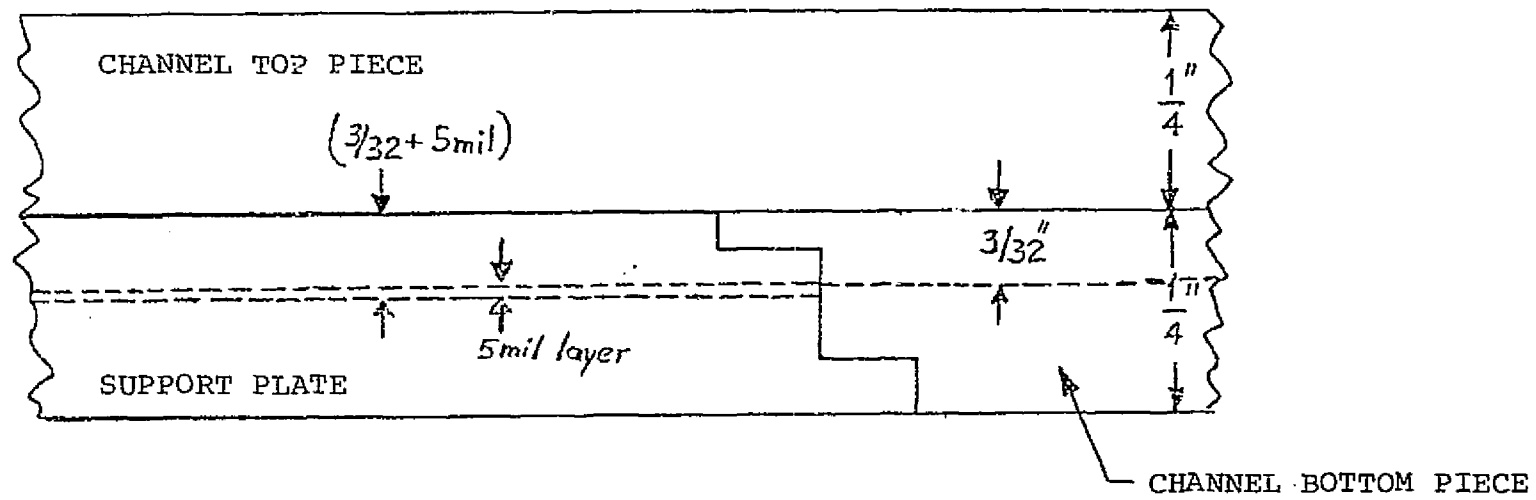
DETAILED DRAWINGS OF CHANNEL SORBER

OVERALL LAYOUT

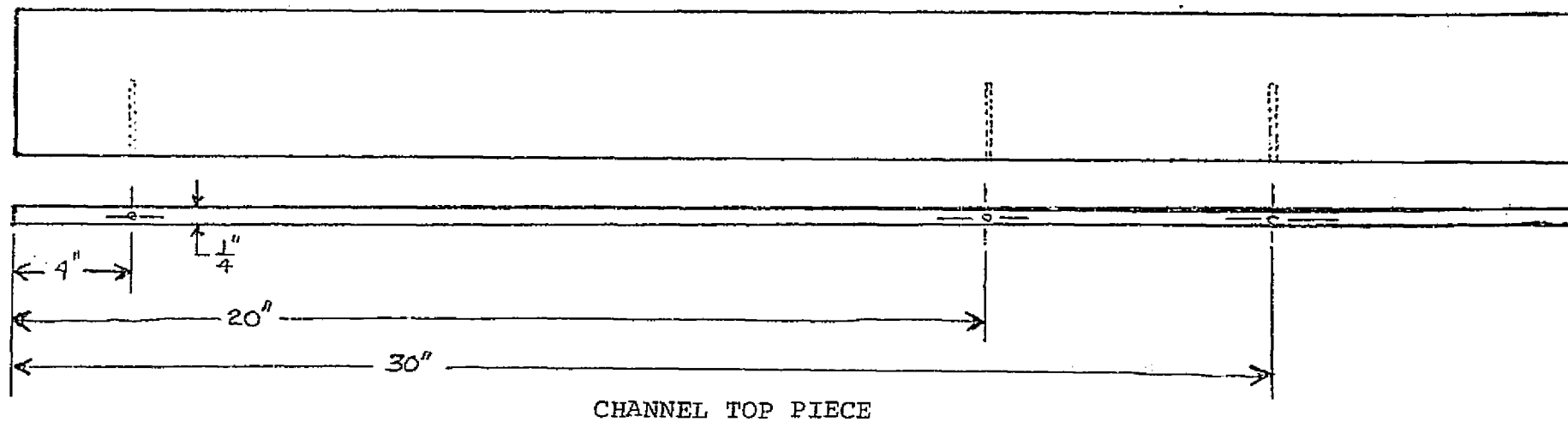
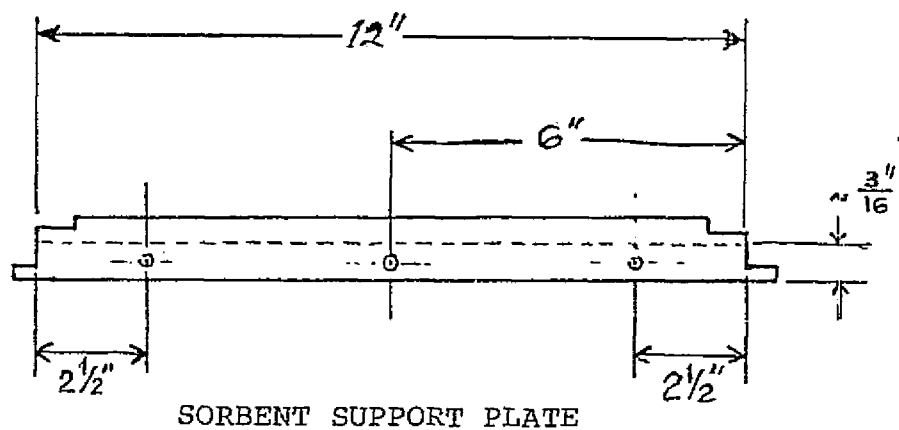
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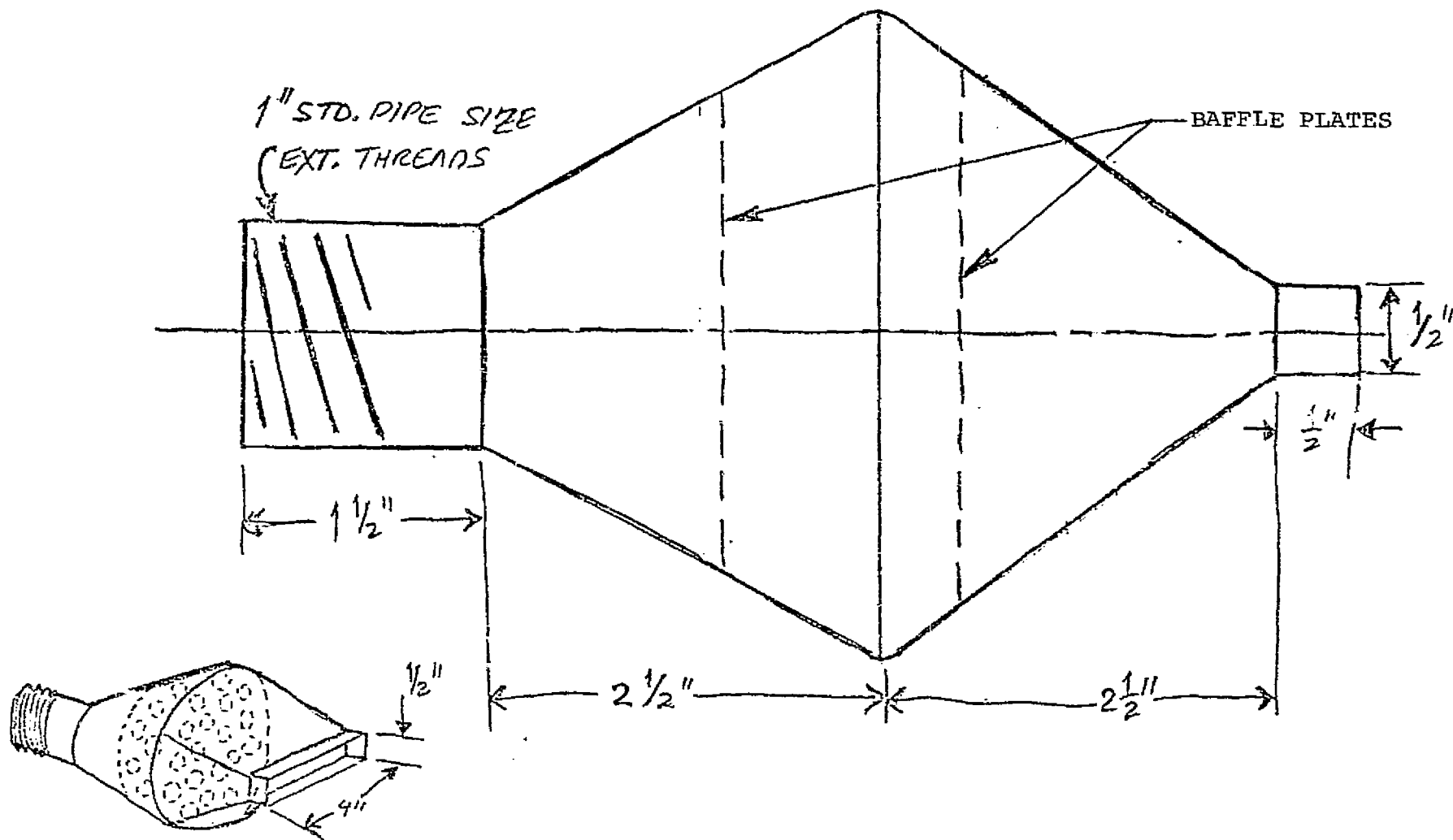
ASSEMBLY OF SUPPORT PLATE AND CHANNEL PIECES



POSITION OF 1/16" DIAMETER THERMOCOUPLE HOLES  
 DRILLED TO CENTERLINE IN PLATE SECTION & CHANNEL TOP PIECE



MIXING CHAMBER AND  
EXIT TRANSITION PIECE: RECTANGULAR CHANNEL TO 1 INCH PIPE  
MATERIAL: STAINLESS STEEL SHEET METAL



ENTRANCE TRANSITION PIECE  
MATERIAL: SHEET ALUMINUM

